evaluated here. The guessing method has been shown to work for very simple examples, but in general it will not work for more complicated examples [i.e., zinc blende as in (32)]. Approximations can be made, of course, by neglecting certain boundary conditions, or by matching Ψ at only one point, or by using 1-D analogs. These are only crudely representative, however, of the correct solution. After all, the surface states are extremely sensitive to the boundary conditions in the surface-termination region. A definitive and realistic computation of surface states on a 3-D crystal has not yet appeared, in the opinion of the authors. In a sense, surface-state physics is 10–15 years behind solid-state (or bulk) physics. The reason for this is the lack of symmetry in the surface region; the free surface is a huge planar defect. At present very little is known experimentally about its topography and energy structure. Even less is known about *interface* regions [e.g., Si-SiO interface, metal-semiconductor interface, electrolyte-semiconductor interface, etc.], because LEED and other tools cannot be applied there.

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Photostimulated Thermoluminescence in Additively Colored KCl

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Thermoluminescence is observed in additively colored alkali-halide crystals following illumination at low temperature with light of wavelength in the absorption bands of the sample (F, K, and L bands) and subsequent heating. In this method one deals with only one type of carrier (electrons) and with one type of activator (negative-ion vacancies). Thus, the nature of the trap and the trapping mechanism can be studied under circumstances which avoid the complications intrinsic to the thermoluminescence of x- or γ-irradiated samples. At least two types of traps are present besides the F' in KCl in the temperature range 55–300°K. Hence the quantum yield of the $F \rightarrow F'$ optical conversion is less than 2. No traps were found associated with fresh dislocations. Two different mechanisms of trap filling have been observed, one through the conduction band, and another through tunneling from the lower excited state of the F center to a neighboring trap.

1. INTRODUCTION

In alkali-halide crystals, thermoluminescence is usually studied in samples which have been irradiated with ionizing radiation (x,γ,e^-). The emission glow curves which result when the sample is subsequently heated are often subject to ambiguous interpretations, in spite of the efforts to correlate the glow peaks to the intensity changes of given absorption bands, EPR spectra, etc. This is due to the fact that one deals with many unknown parameters at the same time, e.g., traps, carriers, activators, and killers. In the literature, one can still find unsolved questions on basic points, such as the nature of the carrier involved. A useful simplification is obtained when a crystal previously irradiated at a relatively high temperature with x or γ rays, in order to obtain color centers and activators, is stimulated at a lower temperature with monochromatic light.[1–6] Even in this case, however, the nature and the concentration of activators remain largely unknown, because the crystal contains different kinds of color centers and the high-energy radiation may introduce a variety of traps whose properties mask the effect of the intrinsic traps and of the traps due to known color centers.

We propose here an experiment which provides the simplest way to study the thermoluminescence process in alkali-halide crystals, thereby avoiding all the complications intrinsic to x- or γ-irradiated samples. Let us take an additively colored crystal, properly quenched so that only F centers are present. The sample is cooled in darkness down to a temperature T_0 and then illuminated with monochromatic light of wavelength λ_s corresponding to a wavelength in the absorption bands due to the F centers (F, K, or L bands); a fraction of the electrons excited by the illumination leaves the negative-ion vacancies and is captured by the traps of the crystal. During the subsequent heating, the

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[1] A. E. Stoddard, Phys. Rev. **120**, 114 (1960).
[2] A. A. Braner and M. Israeli, Phys. Rev. **132**, 2501 (1963).
[3] B. Bosacchi, R. Fieschi, and P. Scaramelli, Phys. Rev. **138**, A1760 (1965).
[4] R. Fieschi and P. Scaramelli, Phys. Rev. **145**, 622 (1966).
[5] P. Scaramelli, Nuovo Cimento **45B**, 199 (1967).
[6] P. R. Crippa, C. Paracchini, and J. Felszerfalvi, J. Phys. Soc. Japan **24**, 92 (1968).

traps empty at their characteristic temperature, and the released electrons recombine with the activator's negative-ion vacancies (α centers), emitting infrared photons (F luminescence). An apparent difficulty results from the fact that α centers in x-irradiated samples are unstable at high temperature.[7] One should bear in mind, however, that the α bleaching process, in this case, is due to recombination with V-type centers, which are absent in the additively colored crystals. We assume that a fraction of the α centers persists also after the F' thermal bleaching; this assumption agrees with the results of Hirai and Ikezawa,[8] who find F luminescence due to the recombination of conduction electrons with α centers up to room temperature. (See also the results obtained by Barr and Dawson,[9] who find the values 1.15–1.45 eV for the activation energy for extrinsic anion diffusion in KBr.) Because of the low illumination employed in the experiment and the sensitivity of the experimental apparatus, many cycles of measurements can be carried out on the same sample [Fig. 1(a)] before ageing effects appear. A plot of the intensity of a given glow peak as a function of the stimulation wavelength yields the stimulation spectrum [Fig. 1(b)].

As to the recombination process, one cannot exclude, in principle, the possibility that thermally free electrons recombine also with activators other than the negative-ion vacancies. The infrared emission in the range of about 1 μ, however, is predominant. This agrees with the observation of many authors that the electrons in the conduction band recombine with the negative-ion vacancies, emitting the characteristic F luminescence.[8] The radiative recombination probability is strongly temperature-dependent, so that the comparison of the

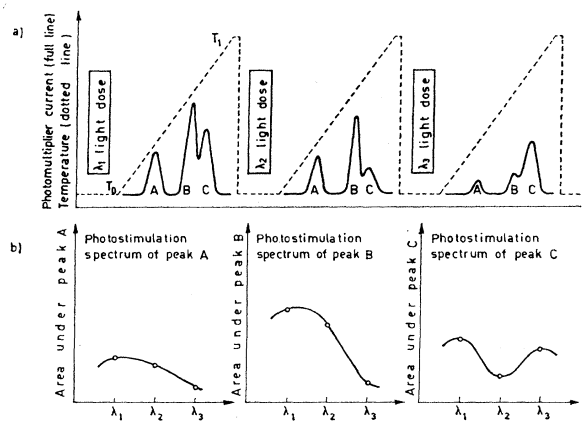

FIG. 1. Method for obtaining the photostimulation spectra of the various glow peaks. The areas under every glow peak are plotted versus the stimulating wavelengths.

[7] G. Chiarotti, G. Giuliani, and D. W. Lynch, Nuovo Cimento 17, 989 (1960).

[8] M. Hirai and M. Ikezawa, J. Phys. Soc. Japan 22, 810 (1967).

[9] L. W. Barr and D. K. Dawson, in Proceedings of the International Symposium on Color Centers in Alkali Halides, Rome, 1968, p. 22 (unpublished).

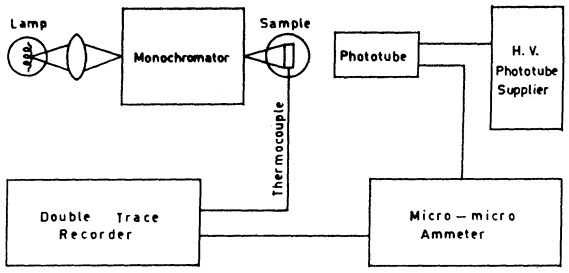

FIG. 2. Block diagram of the apparatus.

different glow bands of a given thermoluminescence curve does not indicate directly the number of the electrons trapped in the corresponding traps; for instance, a high-temperature glow peak corresponds to a higher number of traps than does a low-temperature glow peak of the same intensity.

2. EXPERIMENTAL

The apparatus is sketched in Fig. 2. The sample, held in a cryostat, could be rotated in front of a monochromator exit or in front of an ir photomultiplier. The temperature of the crystal could range from 55 to 300°K with a constant heating rate of 36°/min.

A Philips 7158 lamp was used as source of light. The light was monochromatized with a Zeiss MM 12 double monochromator utilizing a bandwidth that varied from 1 to 5 mμ. The light emitted from the crystal was detected by a Philips 150 CVP photomultiplier sensitive from 400 to 1100 mμ (S1 response) that was cooled to 80°K. The cooling reduced the dark current level by about 5×10^3 without changing the sensitivity appreciably. The phototube current was measured with a Keithley model 414 micromicroammeter and registered on a Speedomax recorder.

The samples were obtained from Harshaw Chemical Co. or grown by the Kyropoulos method in dry-nitrogen atmosphere. In some cases the crystals were also zone refined.[10] The coloration was obtained with the standard additive or electrolytic method. KCl was chosen because its F luminescence is detectable with an ir phototube. The crystals were cleaved in $8\times6\times1$-mm slices and quenched in the dark from 500°K. Absorption-spectra determinations were always performed after the heat treatment in order to control the elimination of the F aggregate centers and to determine the F-center concentration.

The photon density incident on the crystal was evaluated by means of a photoresistance (Philips RPY 17), substituted for the sample. This result was checked with a photodiode H.P. 4220. The number of photons emitted from the crystal was evaluated with the phototube after correcting for the geometrical and optical collection efficiency. In each case we based our calculation on the data given by the manufacturer: In

[10] R. Cappelletti, V. Fano, and M. Scalvini, Ricerca Sci. 38, 668 (1968).

our experiment the lowest light level detectable was about 10^6 photons/sec cm^2. Normally the photostimulation dose was obtained with a monochromator slit width of 0.5 mm for 2 min. This corresponds, at 410 mμ, to about 10^{13} photons falling on the crystal. In order to compare properly the stimulation efficiency of different monochromatic light, the glow peak must be corrected by a factor depending on the wavelength of stimulation, according to the emission spectrum of the lamp.

3. RESULTS AND DISCUSSION

Typical glow curves for illumination at 55°K are shown in Fig. 3. The results represented by curve *a* were obtained after illumination at 410 mμ corresponding to the maximum of photoconductive response in KCl, hence are caused by traps filled by carriers from the conduction band. Curve *b* was obtained with *F*-light photostimulation (540 mμ) and, as will be explained below, indicates that there is a trap-filling mechanism which does not involve the passage of electrons in the conduction band. In both cases, three main glow bands are evident at 115, 225, and 285°K; thus three kinds of traps are filled by the two different mechanisms.

Previous works[3,11] suggest that the glow peak at 225°K corresponds to the temperature range where thermal bleaching of the F' center takes place. We have noticed that illuminating the crystal with F' light at 55°K, after photostimulation, decreases the 225°K peak with respect to that obtained by the photostimulation alone.[5] These facts prove that this peak is to be attributed to the F' trap.

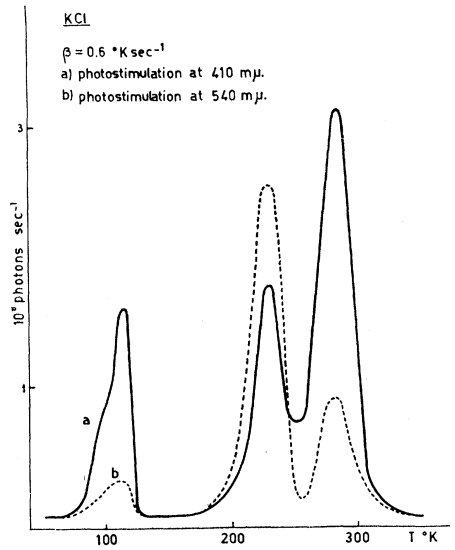

FIG. 3. Glow curves obtained after illuminating a KCl crystal at 55°K with the maximum photoconductivity wavelength (410 mμ, curve *a*) and with the maximum *F* absorption (540 mμ, curve *b*). The curves are corrected for the spectral emission of the lamp.

When optical stimulation is performed at a temperature where F' centers are thermally stable, it is known that, under optical stimulation with light which ionizes the *F* centers, the $F \rightarrow F'$ conversion takes place and the *F* centers themselves act as traps. One expects that the *F* centers are by far the predominant traps. The glow curve in Fig. 3 shows, on the contrary, that in the temperature range 55–300°K at least three types of traps are effective. This demonstrates that the usually accepted value of 2 for the quantum yield of the $F \rightarrow F'$ optical conversion is certainly wrong at the initial stage of the process, since an appreciable fraction of the *F* photoelectrons does not yield F' centers, but instead goes to traps other than *F* centers.

As to the other glow peaks, it is not a simple task to assign them to specific imperfections. Since the number of traps involved may be very low, a real crystal has many possible imperfections, e.g., metal impurities, point defects, and dislocations that can contribute to glow peaks. Preliminary measurements show the deformation by bending does not produce new glow peaks; hence in the present temperature range no electron traps are associated with fresh dislocations.

An estimate of the number of traps filled during a photostimulation has been obtained from the number of photons either incident on the crystal or emitted during the thermal glow. If n_1 is the total number of photons incident on the crystal during a photostimulation cycle, the number of filled traps is given by

$$n_1(1-e^{-\mu x})[1-\eta(\lambda)],$$

where μ is the absorption coefficient at the photostimulation wavelength, x is the thickness of the crystal, and $\eta(\lambda)$ is the relative luminescence quantum yield. In this way the number of filled traps in the range 55–300°K with a single photostimulation (120 sec at 410 mμ) is found to be 7×10^{13} cm^{-3}.

This result was checked by measuring the number of photons emitted during a glow peak, and taking into account the *F*-luminescence yield as a function of temperature.[8] For the peaks at 115, 225, and 285°K, we obtain a filled-trap density of 3×10^{11}, 4×10^{12}, and 3×10^{13} cm^{-3}, respectively.

A further qualitative check was performed by measuring the decrease of the *F* absorption band after long illumination (3 h) of the crystal. We again found that the number of filled traps was of the same order as that determined above.

Figure 4 gives the intensities of the three glow peaks as a function of the photostimulation dose with 410-mμ light. The initial slope of these curves is proportional to the product of the capture cross section and the concentration of the traps. The peak at 285°K saturates, while the other two peaks increase linearly even with an illumination dose 150 times longer than that generally employed (120 sec). This tells us that the total

[11] D. Dutton and R. J. Maurer, Phys. Rev. **90**, 126 (1953).

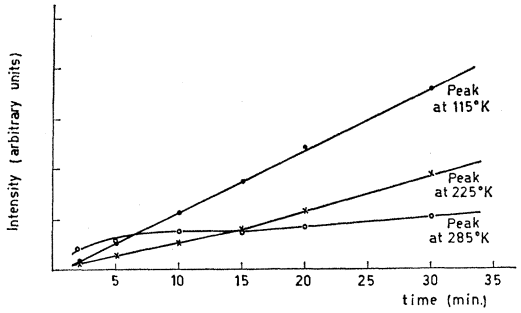

FIG. 4. Intensities of the glow bands as a function of the illumination time, with light at 410 mμ. The light flux on the entire crystal is of the order of 10^{11} photons/sec.

trap concentration responsible for the peak at 285°K is of the order of 5×10^{13} cm^{-3}, while that responsible for the peak at 115°K is larger than 10^{13} cm^{-3}. Obviously, the concentration of F' centers (225°K peak) must be the same as that of the F centers in the crystal.

It is clear that with these concentrations the optical filling of the traps had no detectable effect on the absorption spectrum. It should be noted that the optical detection of low concentrations of traps is particularly difficult for shallow traps with broad absorption bands.

The photostimulation spectrum from 380 to 640 mμ shows two maxima for all three peaks: The first, at 410 mμ, corresponds to the highest photoconductivity energy; the second, at 560 mμ, coincides with the maximum of the F-band absorption (Fig. 5). This assures us that all the traps involved can be filled by the motion of carriers through the conduction band or by tunneling from the excited $2p$ state of the F center. Tunneling is particularly evident for the peak at 225°K. This is also shown by other recent measurements.[12,13] The photostimulation spectra of peaks at 115 and 225°K are obtained with a light dose of 2 min. It should be noted that, in order to avoid saturation effects which

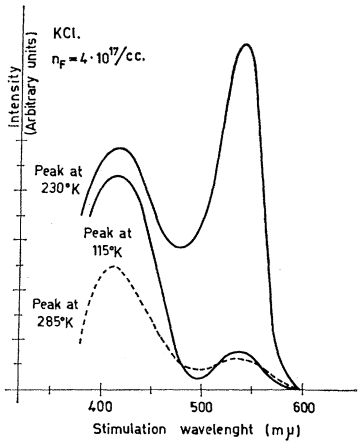

FIG. 5. Photostimulation spectra of the glow bands. The light dose used for obtaining the spectrum of the 285°K peak was three times smaller than that used for the 115 and 225°K peaks.

[12] G. Chiarotti and U. M. Grassano, Nuovo Cimento **46B**, 78 (1966).
[13] T. Ishii and T. Endo, J. Phys. Soc. Japan **24**, 254 (1968).

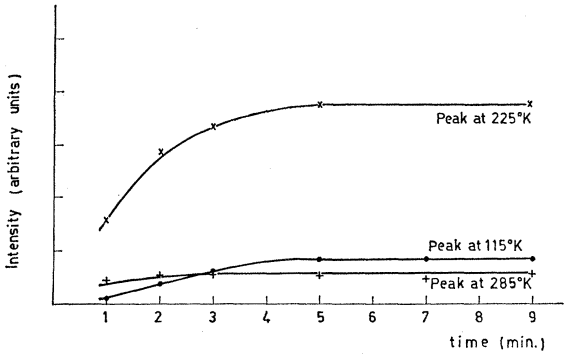

FIG. 6. Intensities of the glow bands as a function of the illumination dose at 540 mμ. Because of the lamp emission, the light flux is in this case 10 times larger than that of Fig. 4.

would distort the stimulation spectrum, the 285°K peak was studied at a lower stimulation light dose.

Figure 6 presents the intensities of the three peaks versus the photostimulation dose at 540 mμ. The saturation effect is now present for all the glow peaks. This is consistent with the fact that tunneling takes place only at the traps near the excited F center, while all the traps of the crystal can be filled by carriers in the conduction band.

4. CONCLUSIONS

Thermoluminescence is obtained in additively colored alkali-halide crystals by means of illumination with light into the absorption bands of the sample. Carriers excited by light are trapped at metastable states of imperfections. Subsequent heating frees the carriers and allows them to recombine with negative-ion vacancies, with the emission of an F-luminescence photon.

By this method one can study the traps in an additively colored crystal, thereby avoiding the complications intrinsic to the thermoluminescence of x- or γ-irradiated samples.

In the temperature range 55–300°K, besides the glow peak associated with F' traps ($T_{max}=225$°K), two other glow peaks appear at 115 and at 285°K, indicating that the quantum yield of the $F\rightarrow F'$ optical conversion is less than 2.

The comparison of the photostimulation spectrum with the photoconductivity spectrum reveals that traps can be filled either by electrons from the conduction band or by tunneling from the excited state of the F center. In the latter case, the number of filled traps saturates at concentrations of the order of 10^{11}, 10^{14}, and 10^{13} traps per cm^3 for the peaks at 115, 225, and 285°K, respectively, showing that only a limited number of traps can be filled by tunneling from the excited F center.

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