PHYSICAL REVIEW VOLUME 120, NUMBER 1 OCTOBER 1, 1960

Effects of Illumination Upon Sodium Chloride Thermoluminescence

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(Received May 17, 1960)

Illumination of a sodium chloride crystal at liquid nitrogen temperature after x-ray irradiation at a higher temperature or higher temperature annealing has two effects upon its thermoluminescence: Glow peaks stable at the temperature of x-ray irradiation or annealing are diminished in intensity. Missing glow peaks, unstable at the temperature of x-ray irradiation or annealing, reappear in the glow curve. Both effects are greatest for illumination in the *F* band. The results are not consistent with existing models of the thermoluminescence process.

INTRODUCTION

EXPERIMENTS on the thermoluminescence of sodium or potassium chloride have been made by many investigators, frequently with contradictory results. Models of the thermoluminescence process which have been used to account for these experiments are of two types. The model of Randall and Wilkins[1] involves a number of electron excess centers, each of which contributes a glow peak in thermoluminescence. Models involving a single electron excess center are exemplified by that of Bonfiglioli, Brovetto, and Cortese.[2] In this model, properties of electron deficient centers give rise to a many-peaked glow curve. Illumination of sodium chloride before observing its thermoluminescence results in two complementary effects to be described in this paper. Either of the two types of models is seemingly contradicted by one or the other of these illumination effects.

If sodium chloride is cooled to near liquid nitrogen temperature, irradiated with x-rays and then warmed, a number of glow peaks are observed in the temperature range to 400°C. If the x-ray irradiation is made at a higher temperature and the sample returned to near liquid nitrogen temperature in the dark, only those glow peaks occurring at temperatures above that of irradiation are then observed. Appropriate illumination of the sample after it is returned to liquid nitrogen temperature from a higher temperature of x-ray irradiation is found in this study to change the expected glow curve in two ways: First, the glow peaks normally observed above the temperature of x-ray irradiation are diminished in intensity. Second, the missing glow peaks below the temperature of x-ray irradiation now also appear in the glow curve. The first effect may be termed "bleaching," the second "excitation."

Measurements of the "bleaching" of glow peaks in a crystal x ray irradiated at dry ice temperature were made as a function of the wavelength of illumination in the range 400 to 1200 mμ. A decrease in thermoluminescence was observed for all glow peaks above the irradiation temperature, with maximum bleaching of each by light in the *F* band. The sample was next annealed, following x-ray irradiation, to remove all but the highest temperature glow peak. "Excitation" of the lower temperature peaks was then observed to result from illumination of the sample in the *F* band at liquid nitrogen temperature.

The bleaching effect is in accord with models of thermoluminescence involving a single type of electron excess center. The excitation effect, on the other hand, is predicted by a model with several electron excess centers. Neither of the types of models seems to account for both the bleaching and excitation effects.

EXPERIMENTAL

A single 0.5×5×5 mm cleaved crystal from a Harshaw crystal of sodium chloride was used throughout this study to obtain reproducibility. As is known,[3] the glow curve of a crystal heated and cooled many times is not the same as that of a virgin crystal. The results reported here pertain to a temperature cycled crystal.

Thermoluminescence was observed with an almost linear heating rate of approximately 2°C per second. The sample was placed in a recess in an internally heated copper block and fitted against the lower end

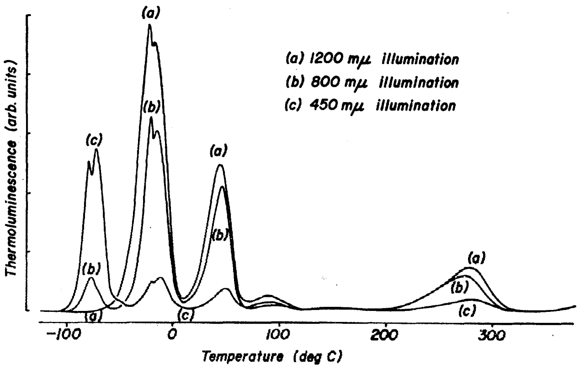

FIG. 1. Thermoluminescence of sodium chloride after x-ray irradiation at dry ice temperature and illumination at selected wavelengths at liquid nitrogen temperature.

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[1] J. T. Randall and M. H. F. Wilkins, Proc. Roy. Soc. (London) **A184**, 366 (1945).

[2] G. Bonfiglioli, P. Brovetto, and C. Cortese, Phys. Rev. **114**, 951, 956 (1959).

[3] A. Halperin, N. Kristianpoller, and A. Ben-Zvi, Phys. Rev. **116**, 1081 (1959).

of a fused quartz light pipe extending vertically to a fused silica windowed photomultiplier. The phototube signal passed an impedance matching amplifier to the vertical axis of an X-Y recorder. The horizontal axis of the recorder was driven by a thermocouple attached to the copper heater block.

X-ray irradiations of 15-min duration were made with a Picker army field unit operated at 30 kv and 4 ma. The sample was maintained either at dry ice temperature or at room temperature during irradiation according to the experiment in progress.

The sample was illuminated by monochromatic light from a Beckman monochromater with a carbon arc source. The monochromater slits were adjusted for approximately equal illumination through the wavelength range 400–1200 mμ, as judged by the current drawn from a silicon solar cell at the sample position. Cell response was corrected for wavelength according to the manufacturers' specifications.

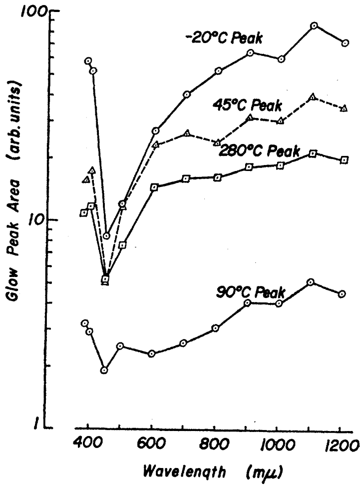

FIG. 2. Bleaching of sodium chloride glow peaks stable at dry ice temperature by illumination in the wavelength range 400–1200 mμ.

The bleaching effect was studied in the following sequence of procedures: (1) The sample was irradiated by x rays at dry ice temperature. (2) It was transferred quickly to a plate at liquid nitrogen temperature in the position of the emergent beam of the monochromater. (3) The wavelength of illumination was selected and the sample illuminated for 5 min. (4) The sample was transferred quickly to the liquid nitrogen cooled heater block of the thermoluminescence apparatus and its glow curve obtained. The sequence was repeated for a number of different wavelengths.

The excitation effect was studied in the same way, changing only the first step of the sequence to: (1a) The sample was irradiated by x rays at room temperature. (1b) It was annealed at 100°C for 6 min. Steps 2, 3, and 4 of the bleaching experiments were then repeated at a number of illumination wavelengths.

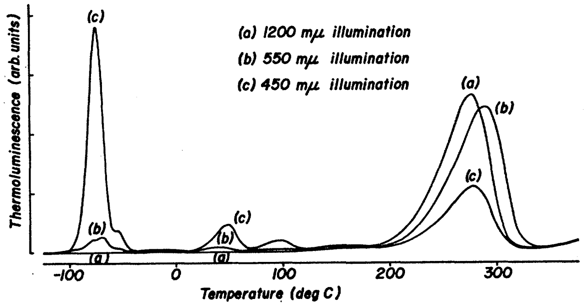

FIG. 3. Thermoluminescence of x-ray irradiated sodium chloride after annealing at 100°C and illumination at selected wavelengths at liquid nitrogen temperature.

RESULTS

Figures 1 and 2 present the results of the bleaching experiments. Glow curves of the sodium-chloride sample after illumination at selected wavelengths are shown in Fig. 1. Curve (a), for 1200 mμ illumination, is the same as that observed following x-ray irradiation at dry ice temperature with no illumination. All of the glow peaks present in this glow curve are decreased in intensity in curves (b) and (c) by illumination with light of shorter wavelength. The second figure contains the areas of these peaks as obtained from Fig. 1 and from similar glow curves obtained following illumination at additional wavelengths.[4]

In contrast to the general behavior in Fig. 1, the glow peak at −75°C increases in curves (b) and (c). Growth of this glow peak represents the excitation effect of illumination. Were the sample x ray irradiated at liquid nitrogen temperature, the −75°C glow peak would be observed in its thermoluminescence. Instead, the sample was irradiated at dry ice temperature where the peak is thermally unstable and is not observed. Illumination at liquid nitrogen temperature after x-ray irradiation on dry ice reinstates the glow peak in the samples' thermoluminescence. Glow peaks at lower temperature than that of x-ray irradiation may be excited in this way, while those at higher temperatures are bleached.

Figures 3 and 4 contain the results of the excitation experiments. The sample was annealed at 100°C in these experiments to remove all but the highest temperature glow peak observed. Curve (a) of Fig. 3 is the same as that observed after annealing, with no illumination. No glow peaks below 100°C are present. Curves (b) and (c), observed after illumination, show the excitation of glow peaks below this temperature, and bleaching of the main peak above this temperature.

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[4] In all cases of a doublet structure in a peak the total area under the doublet was measured as the area of the peak. The components of the −20°C peak did not vary much in intensity in the bleaching experiments. Considerable variation in the relative intensities of the −75°C peak components was observed in the excitation experiments, however. These glow peak doublets probably correspond to the emission band doublet reported by Halperin in reference 3.

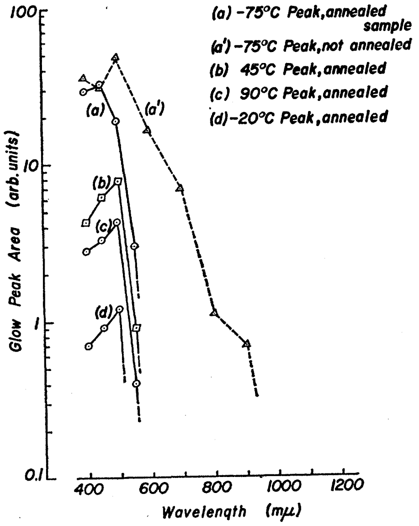

FIG. 4. Excitation of sodium chloride glow peaks, following removal with 100°C anneal, by illumination in the wavelength range 400–1200 mμ at liquid nitrogen temperature. The dashed curve represents excitation of the −75°C glow peak in a sample which was not annealed, but was irradiated by x rays at dry ice temperature.

Bleaching of the 280°C peak in these experiments is similar to that shown in Fig. 2.

The areas of the excited glow peaks in Fig. 3 and in similar glow curves at additional wavelengths of illumination are shown in Fig. 4. The −75°C peak was excited in both the excitation and bleaching experiments. Its growth in the bleaching series is shown as curve (a′) in Fig. 4 for comparison with its growth in the excitation series, curve (a).

DISCUSSION

Current models of thermoluminescence may be divided into two categories—models in which the defect states involved are a single electron excess center and several electron deficient centers, and models involving several electron excess centers.

In the single electron excess center models the observed number of glow peaks are ascribed to an equal number of electron deficient centers. The model of Bonfiglioli *et al.*[2] assigns different cross sections to the electron deficient centers for capture of electrons thermally released from the electron excess center to the conduction band. The lowest temperature glow peak observed arises from capture of electrons by the center with largest cross section. Centers with increasingly smaller cross section give rise to a succession of glow peaks with increasing temperature.

Halperin[5] mentioned a model due to Katz involving the same centers. However, electrons are assumed thermally excited from the valence band to electron deficient centers, rather than from the electron excess center to the conduction band. Light emission accompanies capture of the resulting valence band holes by the electron excess center.

Randall and Wilkins[1] assume glow peaks to arise from the thermal release of trapped electrons distributed in a number of distinct electron excess centers. Increasing temperature releases electrons first from that type of center with lowest activation energy, etc.—the types of centers equaling the number of glow peaks. Emission of light accompanies capture of these electrons from the conduction band by unspecified electron deficient centers.

The effect of illumination upon thermoluminescence divides into two effects—bleaching and excitation of glow peaks. Agreement of models involving a single electron excess center with the bleaching effect, or of a model with several electron excess centers with the excitation effect will be discussed first. The fact that the two effects are complementary leads to a discussion of the difficulty of any of the models in accounting for this set of experiments.

Illumination in the *F* band reduces the concentration of *F* centers in the crystal. The primary feature of the bleaching curves in Fig. 2 is the reduction in intensity of all of the glow peaks following *F*-band illumination. This result is expected in single electron excess center models in which this center is the *F* center. Fewer electrons are available from *F* centers for radiative capture from the conduction band of the heated crystal by electron deficient centers. Or, fewer electrons are present as *F* centers for radiative recombination with holes in the valence band of the heated crystal.

The excitation effect is in accord with the model of Randall and Wilkins if it is assumed that the 280°C glow peak remaining after annealing is associated with the *F* center. Lower temperature peaks are associated with other electron excess centers from which all electrons were removed by annealing. Illumination of the annealed sample by *F*-band light at low temperature releases electrons from *F* centers to the conduction band. Some are captured by the other electron excess centers. When the crystal is subsequently heated, each of the electron excess centers again contributes its peak to the glow curve, as observed.[6]

Excitation of the −75°C glow peak by longer wavelength light in the unannealed sample than in the annealed sample [curves (a′) and (a) of Fig. 4] also follows from the Randall and Wilkins model. Centers to be associated with the low-temperature glow peaks, e.g., *R*, *M*, and *N* centers, are ionized by light on the long wavelength side of the *F* band. These centers would contribute electrons to the center associated

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[5] A. A. Braner and A. Halperin, Phys. Rev. **108**, 932 (1957).

[6] Excitation of the −20°C glow peak by illumination of the annealed sample in the *F* band is anomalously small. In this model, the center associated with this peak must be supposed formed with quite different ease by x rays and by conduction band electrons from *F* centers.

with the −75°C peak upon illumination of the unannealed sample.

Difficulty is encountered in fitting both the bleaching and excitation effects to either one of the categories of models. In the single electron excess center models, the number of glow peaks equals the number of electron deficient centers. Only one glow peak remains after annealing. Correspondingly, annealing leaves but one electron deficient center and a residual concentration of *F* centers. Illumination in the *F* band can only reduce the concentration of the remaining electron deficient center and further reduce the *F*-center concentration. The models do not allow for the reappearance of glow peaks, in disagreement with the excitation effect.

Randall and Wilkins' model derives the observed number of glow peaks from a series of electron excess centers. If these are centers recognized in optical absorption studies, differentiated by their wavelengths of maximum absorption, the various glow peaks would not be expected to have the similar bleaching curves shown in Fig. 2. Each glow peak would be bleached most at the wavelength of maximum absorption of its associated center. Other glow peaks would be enhanced at this wavelength by the retrapping of some of the electrons released from the absorbing center. Interpreting the bleaching effect in terms of this model requires that the centers which are assumed to have different thermal activation energies have similar optical absorption curves.

Each of the models was proposed on the basis of rather convincing experimental evidence. Each is to some extent supported by the data presented here. Each is also, however, in conflict with one or the other of the two complementary effects of bleaching and excitation. Several reasons may be suggested for thinking the correct model to be some modification of the Randall and Wilkins type. Recent work by Halperin *et al.*[3] greatly weakens the arguments for a single electron excess center model of the type proposed by Hill and Schwed[7] and Bonfiglioli *et al.*[2] Halperin finds different thermal activation energies for the glow peaks, as observed also in this laboratory by initial rise methods. He also reports a common emission band in most of the glow peaks. As pointed out by Halperin, both of these findings contradict those reported by Hill and Schwed and by Bonfiglioli *et al.* as the basis for their model. Nor do the wavelength of the emission band, and the existence also of other bands reported by Halperin fit well with the single electron excess center model proposed by Katz.

Two possibilities arise to account for the bleaching results in the framework of the Randall and Wilkins model. As shown by Compton and Klick,[8] the *R*, *M*, and *N* color centers are not isolated from one another, but interact under illumination. It may be that the centers involved in thermoluminescence of sodium chloride are coupled to the *F* center under illumination in such a way that the concentration of each is reduced by illumination in the *F* band. A second possibility is suggested by the *F*-band growth study of Mitchell, Wiegand, and Smoluchowski.[9] Growth of the *F* band under x-ray irradiation at room temperature is shown to arise from two centers of perhaps the same atomic description, but different physical properties due to different locations in the crystal. If these centers differ in thermal activation energy, the requirements for a Randall and Wilkins type model to account for the experiments reported here are satisfied for two of the sodium chloride glow peaks.

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[7] J. J. Hill and P. Schwed, J. Chem. Phys. **23**, 652 (1955).

[8] W. D. Compton and C. C. Klick, Phys. Rev. **112**, 1620 (1958).

[9] P. V. Mitchell, D. A. Wiegand, and R. Smoluchowski, Phys. Rev. **117**, 442 (1960).