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Afterglow Decay of CaF_2

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Calcium fluoride crystals, excited by low-energy (≈ 10 kV) electrons, are found to exhibit a weak but persistent afterglow in the temperature range 28–250 °C. The portion of the decay curves between 2.5 and 30 sec for different temperatures of excitation has been analyzed assuming exponential decay laws for each of the several traps presumed to be present in the crystal. Traps of comparatively low depth (in the range 0.49–0.70 eV) which escaped detection by thermoluminescence experiments have been determined in this way. The results show that the value of the frequency factor S, which is about 2.2×10^8 sec^{-1} for excitation in the neighborhood of room temperature (28 °C), is lowered by a factor of 10 for higher temperatures of excitation.

I. INTRODUCTION

Energy storage in solids, as indicated by thermoluminescence (TL) and temperature-dependent afterglow exhibited by phosphors, is believed to be due to the trapping and recombination centers with localized energy states present inside the material[1]; the afterglow decay and TL are thus widely used phenomena for investigating the traps and related processes in luminescent materials. The nature of the decay curve is largely determined by the distribution of traps and recombination centers; the temperature dependence being essentially controlled by the lifetime of the trapping state,[2] $\tau = S^{-1} e^{E/KT}$, where E is the corresponding trap depth and S is the frequency factor. In general, the decay curves within particular intervals of time, temperature, and intensity of excitation are analyzed by assuming a suitable sum of exponential or power-law terms,[1–4] but the interpretation in terms of the physical processes is rather ambiguous, because of the inherent uncertainties in the structure-sensitive properties of the material and the varied possibilities of the processes involved. In spite of such complexities of the phenomena, extensive work carried out with a large number of phosphors has established the essential correctness of the ideas about the role of traps and recombination centers in the phenomenon of afterglow.

The interpretation of the decay curves is handicapped by the limited period of time of decay for which measurements can be conveniently made. The shallow traps are emptied too quickly at ordinary temperatures, and at low temperatures the rate of release of stored energy from the deep traps is so low that the afterglow intensity is too poor for a reliable measurement. Very often an appreciable part of the stored energy is left in the deep traps at the end of the measurement; such traps and the corresponding stored energy are reflected in TL. Evidently, measurements on afterglow decay and TL should yield complementary information about traps present in the material. Further, the observed decay constant and the nature of the decay curves are expected to change appreciably for different temperatures of excitation, particularly as it passes through the various glow-peak temperatures.

There are several methods of estimating the trap depths from decay curve analysis and TL[1,5–8]; except in simple cases of traps of the same nature and single depth, the results obtained by different methods are very often in qualitative agreement only. As a matter of fact, in spite of such extensive work in this field, there has been as yet rather a limited attempt for direct determination of S from measurements of the afterglow decay for different temperatures of excitation of phosphors with complicated distribution of traps.

In the present paper results on the temperature dependence of the decay of afterglow of CaF_2 crystals, excited by low-energy electrons, have been reported. Calcium fluoride, a widely studied nonphotoconducting phosphor, exhibits a weak but temperature-dependent afterglow and shows a number of glow peaks in TL.[9–12] The well-known luminescent properties of the crystal[13,14] make it a very suitable material for a fruitful study of the temperature dependence of the decay curves and enables us to determine the trap depths and the constant factor S from such measurements.

II. EXPERIMENTAL RESULTS

The measurements reported here have been carried out with samples of CaF_2 crystals obtained from Harshaw Chemical Company, U. S. A.; the coloration and related luminescent properties of these crystals have been reported earlier.[14,15] The crystals, having the approximate dimensions of 1 cm × 1 cm × 2 mm, were excited by low-energy electrons (≈ 10 kV) in a specially made cathode-ray tube.[15] The crystal should be kept at different temperatures and its temperature measured with a cal-

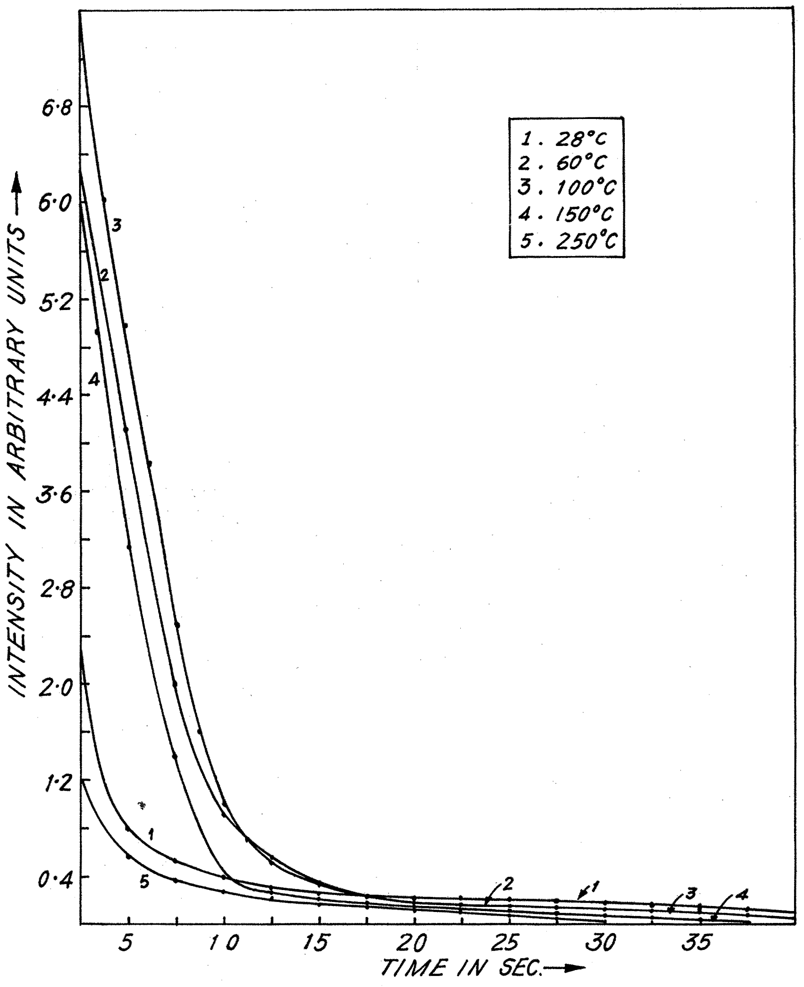

FIG. 1. Afterglow decay of CaF_2 at different temperatures. The crystal was bombarded by electrons (10 kV) for 15 min in all cases.

ibrated thermocouple placed in intimate contact with the crystal and its holder. Crystals were generally irradiated by a nearly steady beam of electrons for about 15 min and the intensity of the afterglow was measured through a quartz window with the help of a 1P28 photomultiplier and the associated recording unit.

The decay of the intensity of afterglow during the period 2.5–30 sec after the stoppage of the excitation could be measured with reliable precision with the experimental arrangement.[15] The measurements have been carried out with several samples of CaF_2 at various temperatures and reproducible results were obtained by several repetitions of each measurement. Some of the typical decay curves obtained for the temperatures of excitation between 28 and 250 °C are shown in Fig. 1. The corresponding TL of the crystal has also been studied[12] and it has been found that while no measurable TL was observed for temperatures of excitation above about 150 °C, the afterglow decay could be measured for temperatures of excitation up to about 250 °C. Further, above 100 °C, the intensity of afterglow decreased with an increase of temperature of excitation and became extremely poor beyond 250 °C.

III. DISCUSSION

The experimental decay curves have been ana-

TABLE I. Trap depths and the associated frequency factors for different temperatures of excitation.

No.	Excitation temperatures (°C)	Slopes (α) (sec^{-1})	E (eV)	S (sec^{-1})
1	(28)[a]	1.27	0.49	2.2×10^8
2	(28)	0.27	0.53	2.2×10^8
3	(28)	0.042	0.59	2.2×10^8
4	60	0.33	0.59	2.2×10^8
5	(60)	0.091	0.61	2.2×10^8
6	100	0.35	0.58	2.4×10^7
7	(100)	0.032	0.65	2.4×10^7
8	150	0.37	0.65	2.4×10^7
9	(150)	0.092	0.70	2.4×10^7

[a] Room temperature.

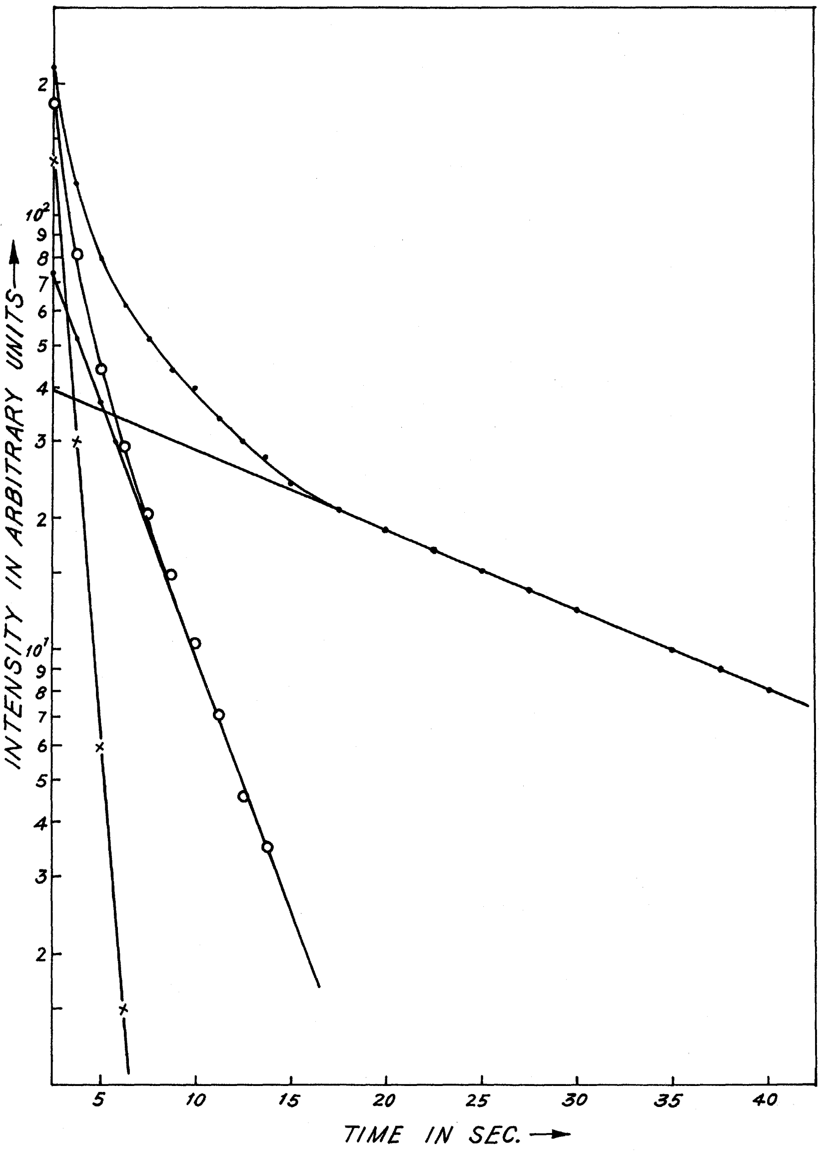

FIG. 2. Afterglow decay of CaF_2 at room temperature (28 °C). The crystal was bombarded by electrons (10 kV) for 15 min.

lyzed in the usual way as a sum of exponential terms, i. e., $I=\sum I_i\, e^{-\alpha_i t}$. The values of α (slopes) for the decay curves at different temperatures are given in Table I. It can be seen that the decay curve at room temperature (28 °C) has been associated with three exponential curves (Fig. 2), each of which is related to the corresponding trap depth; for excitation at temperatures between 60 and 150 °C the decay curves appear to be due to traps with two different depths (an analysis of one such curve at 60 °C is shown in Fig. 3).

From the slopes (α) of the different portions of the decay curves, the trap depth E and its associated frequency factor S, assuming them to be independent of temperature, have been calculated from the relation $\alpha = S\, e^{-E/KT}$. It is, of course, necessary for this purpose to identify the values of α corresponding to the same trap depths for two temperatures of excitation. Since only the traps having lifetimes approximately in the range 2–30 sec are involved in the present measurements, it is possible to choose by trial the temperatures of excitation, such that the trap depth mainly responsible for the last slope of afterglow decay for the lower temperature corresponds to that initial part of the decay for the other temperature. In the present analysis α_3 of the decay curve at 28 °C and α_1 of the decay curve at 60 °C have been taken to be due to same trap depth. In the same way α_1 and α_2 of the decay curves at 150 and 100 °C, respectively, were also related to another single trap depth. Further, in the determination of E and S we have treated the decay curves between 28 and 60 °C and those between 100 and 150 °C as being due

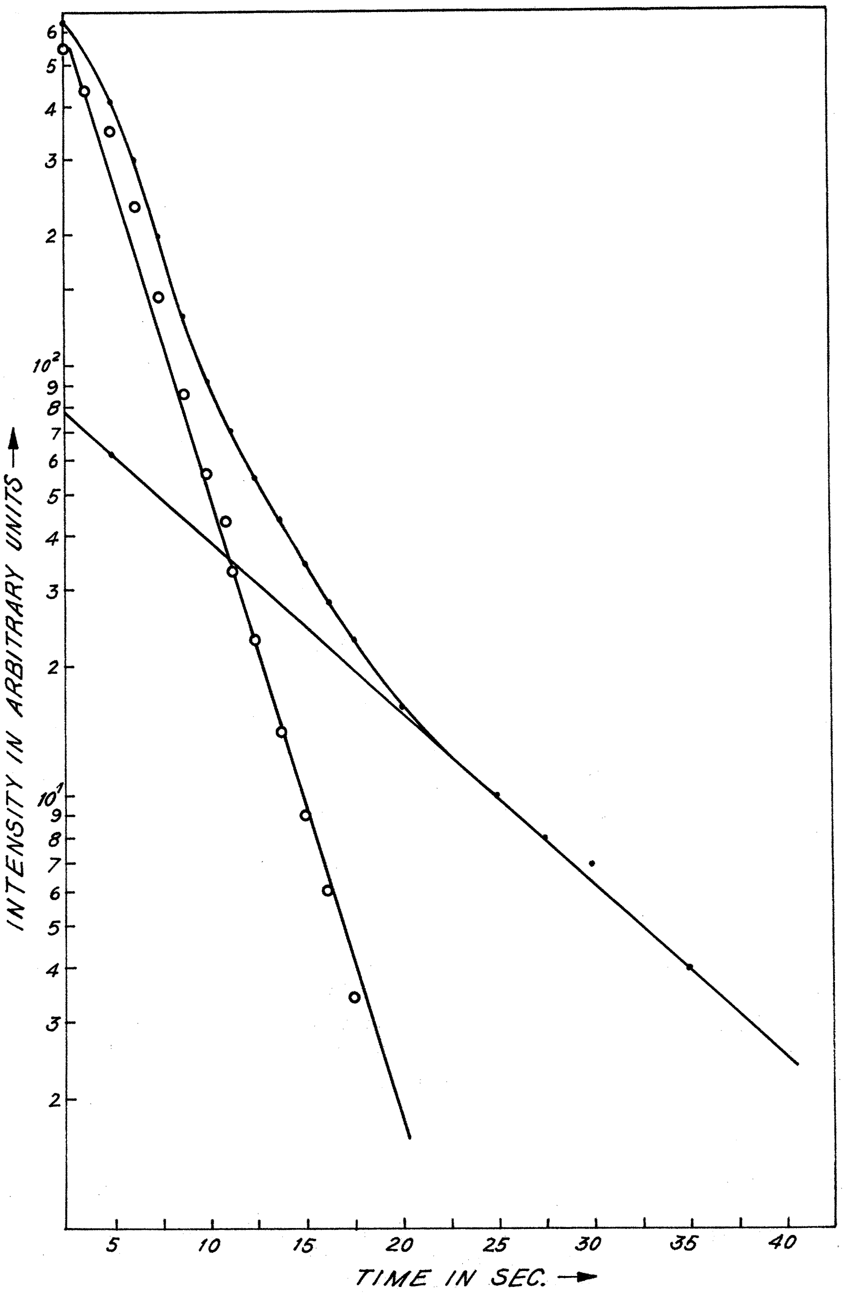

FIG. 3. Afterglow decay of CaF_2 at 60 °C. The crystal was bombarded by electrons (10 kV) for 15 min.

to distinctly different trap distribution. This is justified by the distinct difference in the nature of the glow peaks observed for excitation in the corresponding ranges of temperature.[10,12] The values of trap depths with the corresponding values of S determined in this manner were given in Table I.

It may be pointed out that the trap depths of CaF_2 crystals, determined from the decay curves, were not detected by the method of TL which yielded the deeper traps only. The values of S for excitation in the two temperature ranges mentioned above were found to be (2.2×10^8) and (2.4×10^7) sec^{-1}, respectively. The different orders of magnitude of the value of S were consistent with the idea that the trapping mechanisms of different natures are created by excitation in the corresponding temperature ranges. This viewpoint derives ample support from earlier results on the coloration and luminescent properties of CaF_2 crystals excited by low-energy electrons[14,15]; distinctly different features in their coloration and their luminescence and TL properties are exhibited by CaF_2 crystals for excitation in different ranges of temperature.

Further, the afterglow decay at 250 °C (Fig. 4)

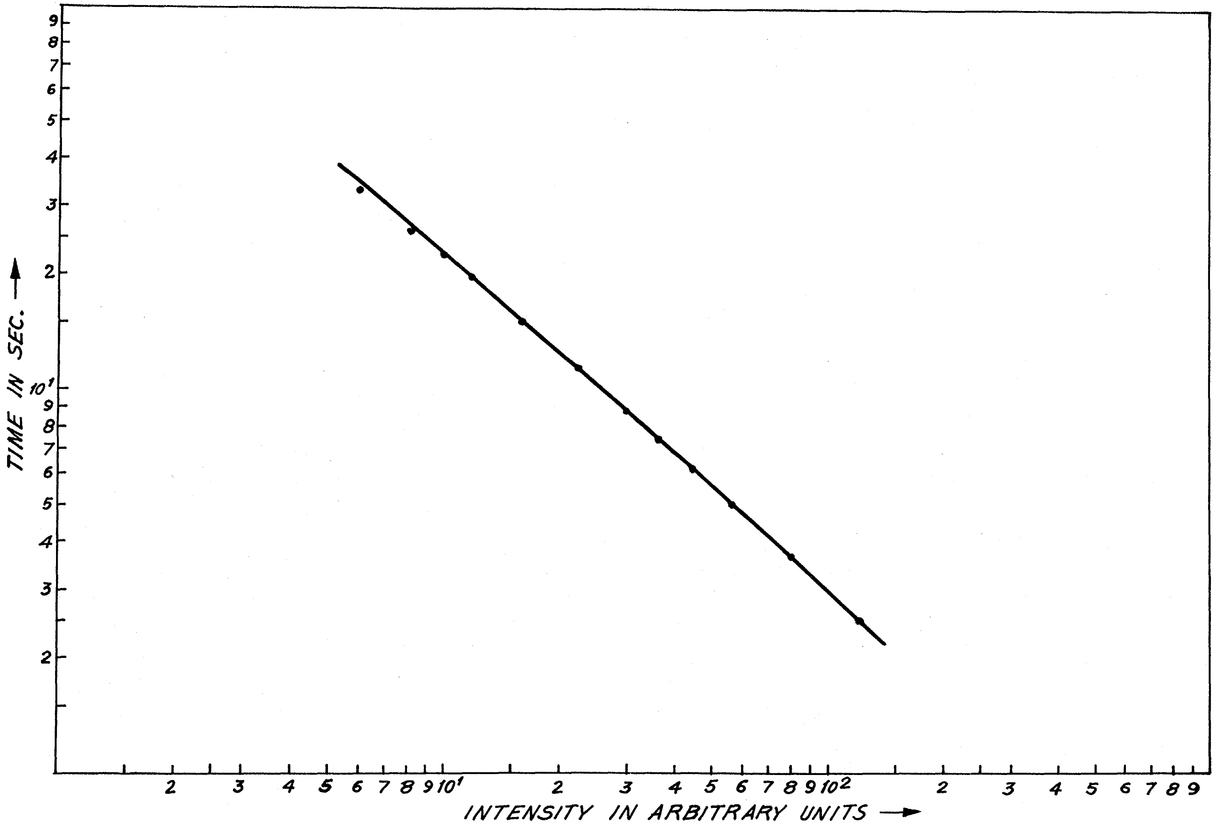

FIG. 4. Afterglow decay of CaF_2 at 250 °C. The crystal was bombarded by electrons (10 kV) for 15 min.

seems to follow a power law $I = I_0 t^{-1.13}$. In this temperature range CaF_2 crystals are known to be densely colored showing α and β bands,[14] and at such temperatures fluorine atoms, i.e., trapped holes, are able to diffuse away from the irradiated zone. It is thus not surprising to find that the afterglow decay law is also different, indicating that the electronic processes occurring during afterglow are more complicated; such complications may arise from either distribution of trap depths or retrapping, or both.

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