STUDY OF THE REDISTRIBUTION OF ELECTRONS AMONG CAPTURE LEVELS IN EXCITED ZnS SINGLE CRYSTALS UNDER THE INFLUENCE OF INFRARED LIGHT

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The redistribution of conduction electrons from deep to shallow levels when irradiated with 1.2 μ infrared light has been studied using curves of thermally stimulated, and photostimulated, conductivity. The influence of repeated capture upon the photostimulated conductivity as a function of decreasing temperature has been evaluated.

It has been shown previously that the conductivity pulses which occur in excited ZnS single crystals when irradiated with infrared light decrease substantially as the temperature is decreased [1]; the inertia of the photostimulated conduction (PSC) process increases at the same time; these effects have not been investigated in detail.

We have investigated the effects leading to a "freezing" of the PSC in greater detail. Samples of ZnS single crystals described in [1] were employed in the investigation. The luminescence and photoconductivity studies were made with the apparatus described in [1].

Illumination of a previously excited crystal phosphor, with infrared light of suitable wavelength, leads to a sudden conductivity increase, to an optical flash, and to radiationless recombination processes, which induce a change in the electron and hole distribution between various levels in the forbidden gap. This redistribution is due to differences in the energy required to liberate electrons and holes from trapping levels at various depths in the forbidden gap, as well as from the subsequent repeated capture processes of charge carriers liberated by the infrared radiation. Repeated capture processes play an essential role for the luminescence as well as for the photoconductivity.

In the case of luminescence, the existence of secondary traps manifests itself in the optical liberation of electrons by repeated phosphorescence effects which occur after the flash; (this flash occurs in a number of phosphors irradiated with infrared light [1-7]). It is generally accepted that repeated capture is also associated with thermoluminescence (thermal de-excitation) [8].

In all the papers cited, repeated capture processes of "optical" electrons by levels from which electrons can be thermally removed into the conduction band have been considered.

Repeated capture of electrons, liberated by infrared radiation from deep levels, by empty shallower traps with E > kT has not been investigated in detail in zinc sulfide phosphors. Also this effect was not investigated in the work dealing with the photoconductivity of ZnS phosphors.

In this paper we shall frequently make use of the curves depicting the thermally stimulated conductivity (TSC) and the PSC described in [1]; we wish to recall that the maxima of the TSC peaks of ZnS phosphors occur at temperatures of 68, -133, and -155 °C, whereas the PSC maxima occur at infrared wavelengths of 3.15, 2.4, and 1.2 μ.

It is known that samples excited at -80 °C, but having electrons only at 68 °C levels, are only susceptible to light with λ = 1.2 μ. Fig. 1 (curve 1) depicts the development of PSC due to 1.2 μ radiation; the phosphor had been excited previously and was kept at -80 °C. In order to obtain an idea of the influence of recombination processes upon the development of the PSC, the development of the luminescence stimulated by the same infrared light was recorded simultaneously. The ordinates of the curves 1 and 2 in Fig. 1 are indicated in arbitrary units. A comparison of the two curves reveals that the PSC process has a greater inertia than the luminescence flash. The figure indicates that the luminescence occurs mainly at the beginning of the irradiation. In this time interval, recombination processes associated with stimulated emission and quenching are the principal processes. The electrons which participate in the recombination processes contribute little to the conductivity [9]. The time of electron incumbency in the conduction band and the probability of their repeated capture increase in inverse proportion to the decline of the luminescence flash; i.e., to the decrease of the number of recombination processes, and this leads to a greater lag on the part of the PSC. The PSC peak is shifted toward larger times relative to the stimulated emission peak; the PSC curve approaches the abscissa axis more gently than the
relaxation curve of the stimulated radiation. After further recombination, the number of electrons ejected into the conduction band is almost equal to the number of newly captured electrons, and this manifests itself in a very slow decline of the PSC with time during prolonged infrared irradiation.

The PSC spectrum of a crystal excited at \(-80^\circ\) C and afterwards cooled to \(-180^\circ\) C has only a peak at \(1.2 \mu\). Peaks at 2.4 and 3.15 \(\mu\) do not occur at \(-180^\circ\) C. The spectrum of the stimulated conductivity therefore coincides in its shape and position with the PSC spectrum observed in phosphors excited at \(-80^\circ\) C, but not cooled below this temperature. However, due to the "freezing" of the conductivity, the conduction current at \(-180^\circ\) C was very small and the sensitivity of the apparatus had to be increased tenfold for these experiments.

The PSC spectrum changes upon prolonged (15 min.) exposure of the 68 \({^\circ}\) C-level electrons to 1.2 \(\mu\) infrared radiation at \(-180^\circ\) C. Apart from the susceptibility to this wavelength, a susceptibility to the wavelengths 2.4 and 3.15 \(\mu\) appears; consequently, in the PSC spectrum there appear additional maxima, which are characteristic of a phosphor excited at \(-180^\circ\) C. The maxima which can be observed upon infrared irradiation with \(\lambda = 2.4\) and 3.15 \(\mu\) correspond to electron liberation from the \(-133\) and \(-155^\circ\) C levels. Thus after irradiation with 1.2 \(\mu\) infrared light an electron redistribution from the 68 \({^\circ}\) level to the \(-133\) and \(-155^\circ\) C levels occurs.

Phosphors excited at temperatures above \(-10^\circ\) C essentially do not exhibit a conductivity pulse from the 68 \({^\circ}\) level upon irradiation with \(\lambda = 1.2 \mu\); an intense conductivity quenching can be observed [1]. In the presence of such quenching, an electron redistribution with infrared irradiation cannot be observed.

Fig. 2. Curves depicting the thermally stimulated conductivity in a ZnS crystal previously excited at \(-80^\circ\) C after irradiation with 1.2 \(\mu\) infrared light at \(-180^\circ\) C (i in relative units, \(t\) in \({^\circ}\) C). Irradiation times: 1) 0.5 min; 2) 1.5; 3) 3; 4) 4.5; 5) 8; 6) 12; 7) 30; 8) 50; 9) 90; 10) 120 min.

Fig. 3. Curves depicting the thermally stimulated conductivity that occurs in a phosphor, previously excited at \(-80^\circ\) C, after irradiation with 1.2 \(\mu\) infrared light at \(-180^\circ\) C (i in relative units, \(t\) in \({^\circ}\) C) with the following relative intensities: 1) 0.6; 2) 0.8; 3) 1; 4) 1.2; 5) 1.4; 6) 1.8; 7) 2.

The number of electrons that are redistributed from deep levels to shallower levels, from which, however, thermal removal at \(-180^\circ\) C is negligible, was estimated from the TSC curves obtained after infrared irradiation at \(-180^\circ\) of a phosphor previously stimulated at \(-80^\circ\) C. Figure 2 shows how the number of electrons in the \(-133\) and \(-155^\circ\) C levels increases with increasing irradiation time. This number is proportional to the areas \(S_T\) under the curves 1–8 in Fig. 2.

In order to compare the effect of the duration of infrared stimulation and the infrared intensity, the electron redistribution to the \(-133\) and \(-155^\circ\) C levels was measured at various irradiation intensities. Fig. 3 indicates that the number of redistributed electrons increases with increasing infrared intensity.

Figures 2 and 3 also indicate that the TSC peak is displaced toward lower temperatures when the number of electrons redistributed from deep to shallower levels increases. Since the \(-133\) and \(-155^\circ\) C levels are smeared-out trapping bands, the deeper levels of the band are first filled, whereupon the center of the distribution shifts toward lower temperatures.