Effect of light on strain-stimulated light emission in ZnS crystals

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An effect of illumination on strain-stimulated light emission by ZnS crystals is detected. The spectral and temperature characteristics of the process are investigated. It is shown that illumination of the sample in the absorption bands of the activator (Cu, Mn) results in a decrease of the number of flashes per unit time (N), whereas light corresponding to band-band absorption ($\lambda \sim 340$ nm) increases N. Possible mechanisms of the effect of light on strain-stimulated luminescence are discussed.

Recent investigations have shown that the photoplastic effect in semiconductors, initially discovered in cadmium sulfide crystals[1-3], is observed in practically all compounds of the II–VI group. Thus, there is at present no doubt that illumination of photoconductors exerts an appreciable influence on their plastic deformation. At the same time, just as in the alkali-halide crystals, luminescence stimulated by dislocations that move as a result of deformation was observed in ZnS.[4]

Comparison of these two phenomena in the same crystals has led to the natural hypothesis that the illumination that causes the photoplastic effect may exert an influence also on the character of the luminescence stimulated by the deformation. The present paper is devoted to an experimental verification of this assumption.

We investigated single crystals of ZnS doped with copper and manganese1) and grown from the melt by the Bridgman method. The samples, measuring 2 × 2 × 4 mm, were so oriented that the glide plane (0001), which is active in the deformation, makes an angle close to 45° with the maximum deforming stress. The crystal was loaded by rectangular mechanical-stress pulses of duration 0.2–20 sec with the aid of an electromagnetic device described earlier[3]. The luminescence was registered with an FÉU-106 photomultiplier and an S-1-37 oscilloscope. The spectral width of the slit used to illuminate the crystal with light from the source through a monochromator was varied from 10 to 100 Å. The light source was a DKSSh-200 xenon lamp. Band filters were used to exclude the effect of the exciting light on the photomultiplier used to register the strain-stimulated luminescence.

EXPERIMENTAL RESULTS

The character of the strain-stimulated luminescence in ZnS crystals turned out to be different than in alkali-halide crystals[5,6]. The loading of colored alkali-halide crystals with a rectangular mechanical stress pulse of amplitude smaller than the elastic limit (σ_{el}) is accompanied by an individual flash of luminescence of ~0.1 sec duration. At stresses larger than the elastic limit, the luminescence of ionic crystals is stationary, i.e., it is observed during the entire loading time.

Loading the ZnS crystals with rectangular mechanical-stress pulses is accompanied by luminescence only at stresses exceeding the elastic limit. A series of light flashes is produced (each series can be characterized by the number of flashes, by the average time between them, and by the amplitude. The duration of each individual flash was of the order of 100 nsec.

In most cases, the amplitudes of the flashes turned out to be close, and then the luminescence could be approximately characterized by the number of flashes per unit time N. The main experimental fact obtained in the present study is that illumination of the crystal changes the value of N, and the character of this change differs in different spectral regions (Figs. 1a and 1b). Figure 2 shows the dependence of the ratio N/N_L on the wavelength λ of the light incident on the sample (N_L is the number of light flashes per unit time when the crystal is illuminated with light of definite wavelength, and N is the corresponding number of flashes in darkness). These data were obtained for the ZnS:Cu crystal. To increase the accuracy, the ratio N/N_L was determined by averag-

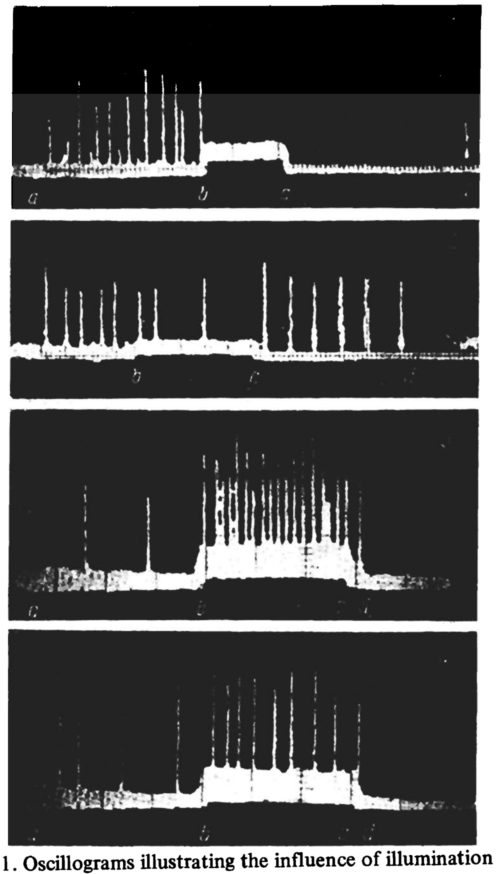

FIG. 1. Oscillograms illustrating the influence of illumination on strain-stimulated flashes of light in a ZnS:Cu crystal. 1 and 2–exciting-light wavelength $\lambda = 360$ nm, light intensity $J_1 > J_2$; 3 and 4–$\lambda = 340$ nm, $J_3 > J_4$; a and d–instants of loading and unloading of the crystal, b and c–instants of turning the light on and off. T = 340°K.

ing 10 measurements. From Fig. 2 we see that the $N/N_L = f(\lambda)$ curve has two clearly pronounced regions with a minimum at a wavelength 340 nm and the maximum at 360 nm. In the region of wavelengths of the order of 340 nm, illumination leads to an increase of the number of flashes, and a decrease was observed at $\lambda \sim 360$ nm.

The ratio N/N_L depends strongly on the intensity of the light incident on the crystal. An increase of the intensity of the light with $\lambda_{max} = 360$ nm leads to a complete vanishing of the light flashes. If the illumination is turned off and the loading of the crystal is continued, then the flashes appear again only after a certain time τ_{del}, the value of which depends on the intensity of the illumination (Fig. 1a). Simultaneously with the luminescence we measured also the residual deformation of the sample. The experiments were performed in darkness, and also at different intensities of the incident light with wavelength 340 and 360 nm. It turned out (Fig. 3) that the number of luminescence flashes and the residual deformation were linearly connected at all values of the incident-light intensities.

The spectral dependence of the ratio N/N_L, obtained in the investigation of a ZnS : Mn crystal, is shown in Fig. 4. Comparing the $N/N_L = f(\lambda)$ curves for zinc-sulfide crystals doped with copper and manganese (Figs. 2 and 4) we can easily see that the positions of their minima coincide, and instead of the 360-nm maximum characteristic of the ZnS : Cu sample, the ZnS : Mn crystal has at least two additional maxima λ_{max}, with approximate values 390, 430, and 520 nm.

Figure 4 shows also the spectrum of the excitation of the intracenter luminescence of Mn^{2+}, obtained for the same samples. A comparison of these curves on Fig. 4 shows that there is a correspondence between the maxima in the photoluminescence-excitation spectra and the maxima on the plot of $N/N_L = f(\lambda)$.

The temperature dependences of the ratio of the number of luminescence flashes under illumination and without illumination in the ZnS : Cu crystals are shown in Fig. 5. The function $N/N_L = f(T)$ (Fig. 5b) was obtained with the crystal illuminated at a wavelength 360 nm, corresponding to the maximum on the spectral dependence of $N/N_L = f(\lambda)$ shown in Fig. 2. The ratio N/N_L decreases monotonically with increasing temperature, and at T = 500°K illumination does not change the number of luminescence flashes.

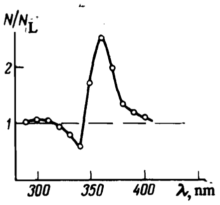

FIG. 2. Dependence of the ratio N/N_L on the wavelength of the exciting light in ZnS : Cu crystal.

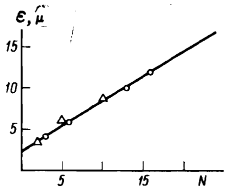

FIG. 3. Residual deformation ε of the ZnS : Cu crystal as a function of the number of luminescence flashes. Experimental data obtained with the crystal illuminated (○) and without illumination (△).

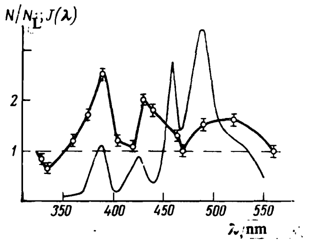

FIG. 4. Spectra of luminescence excitation of Mn^{2+} center (thin line) and of the ratio N/N_L (thick line) in ZnS : Mn crystal.

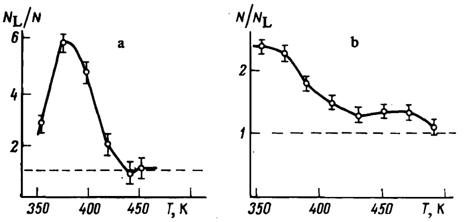

FIG. 5. Temperature dependences of the relative change in the number of luminescence flashes following illumination of a ZnS : Cu crystal with light of λ = 340 nm (a) and λ = 360 nm (b).

The N_L/N dependence obtained by illuminating the crystal at λ = 340 nm (Fig. 5a) is different in form, and corresponds to a minimum on the spectral dependence of $N/N_L = f(\lambda)$. The ratio N_L/N first increases significantly with increasing temperature, reaches a maximum at $T \approx 380$°K, then decreases abruptly and is equal to unity at 430°K.

DISCUSSION OF RESULTS

The previously obtained[4] results indicate quite convincingly that the luminescence flashes produced when a mechanical-stress pulse is applied to a ZnS crystal are of dislocation origin. Each luminescence flash is formed by a large number of dislocations that form a glide plane. The number of luminescence flashes per unit time (N) increases with increasing external stress (σ), corresponding to an increase in the intensity of the developing strain (motion and multiplication of the dislocations).

Within the framework of these concepts, the main result obtained in the present study, namely the spectral dependence of the suppression of the luminescence, is in good qualitative agreement with data on the photoplastic effect in ZnS[7].

Illumination of a plastically-deformed crystal leads to an increase in the resistance to plastic deformation—photohardening. The main maximum on the spectral dependence of the photohardening of ZnS : Cu crystals lies in the same region. This means that light of this wavelength impedes to a maximum degree the motion of the dislocations, placing photobarriers in their path.

In accordance with the dislocation model of the appearance of luminescence flashes in ZnS[4], the hardening should lead to a decrease of the luminescence intensity. This is precisely what is observed in the experiment (Fig. 2). The maximum of the ratio N/N_L, which corresponds to a minimum of luminescence at the given wavelength, lies in the same spectral region (~360 nm) as the maximum of the photoplastic effect.

When discussing the results obtained in the present paper, attention must be called first to the fact that the change in the number of flashes following illumination of the deformed crystal is not due to the influence of the light on the centers that produce luminescence upon deformation, but is an expression of the change produced by the illumination in the characteristics of the motion and multiplication of the dislocations. This follows primarily from the fact that the number of flashes per unit time, which is artificially varied by illuminating the crystal with light having different spectral compositions, is linearly connected with the directly measured residual deformation of the crystal (Fig. 3).

According to data by various authors who investigated the absorption, luminescence, and the photoelectric properties of ZnS:Cu crystals, [8,9], Cu^{2+} centers are produced when these crystals are illuminated at $\lambda_{max} \sim 360$ nm. At the same time, there is no meeting of minds concerning the influence of light in the impurity-absorption band on the Mn^{2+} centers in ZnS:Mn. According to the data by Babe [10], illumination of ZnS:Mn in all the absorption bands of the Mn^{2+} ion does not lead to an increase of the photoconductivity, meaning that it is not accompanied by ionization of the Mn^{2+}. At the same time, in the opinion of Borisenko and Kodzhespirov [11], when a crystal is illuminated in short-wave bands of impurity absorption (λ_{max} 390 and 490 nm), the manganese ion is transformed to an excited state $(Mn^{2+})^*$ with subsequent thermal ionization at $T \geq 300°K$.

The photoelectrons produced upon ionization of the activator are either again captured by the ionized ions of the activator, or by other centers (we shall use for them the general symbol X^+). In particular, according to the data of [9], the X^+ centers in ZnS:Cu can be complexes of the "copper ion + sulfur vacancy" type.

The table lists the final states of the centers when the ZnS crystal is excited in different impurity-absorption bands.

The short-wave maxima on the $N/N_L(\lambda)$ spectral curves for the crystals ZnS:Mn ($\lambda_{max} = 390$ and 430 nm) and ZnS:Cu ($\lambda_{max} \sim 360$ nm) coincide with the corresponding absorption bands in the activated crystals. In the long-wave region, the correspondence between the maxima of the impurity absorption of the manganese ion and the suppression of the luminescence in ZnS:Mn is less clearly pronounced (Fig. 4). We see thus that a decrease in the number of luminescence flashes takes place when the crystal is illuminated in the spectral region where impurity absorption is observed.

The photoplastic effect in ZnS:Mn was not investigated specially, but the data on ZnS:Al show the presence of the "impurity effect" [7].

As to the nature of the photobarriers that influence the motion and multiplication of the dislocations and lead to a decrease in the number of luminescence flashes, it can be proposed that the photobarriers may indeed be the centers produced by illumination at the corresponding wavelength (see the table). One can indicate the possibility of slowing down the dislocations by the excited impurity centers $(Mn^{2+})^*$ that appear when ZnS:Mn is illuminated in the long-wave absorption bands of manganese.

Attention should be called to the relations between the amplitude of the maxima in the intracenter luminescence spectra and the function $N/N_L = f(\lambda)$. In the excitation spectrum of the intracenter luminescence, the amplitudes of the short-wave maxima (390 and 430 nm) are approximately one-third as large as the long-wave maxima. The inverse relation is observed for the function $N/N_L = f(\lambda)$ (Fig. 4). This can indicate that the most effective way of decreasing the number of luminescence flashes is to apply to the ZnS:Mn crystal an illumination that stimulates the formation (in accord with [11]) of ionized Mn^{3+} centers.

The temperature dependence of the ratio N/N_L can be attributed to an increase of the thermally activated surmounting of the photobarriers by the moving dislocations with increasing temperature.

Crystal	Wavelength of light (nm)	Centers	Photoconductivity	References
ZnS : Cu	360	Cu^{2+}, X	+	[8, 9]
ZnS : Mn	390, 430	Mn^{3+}, X	+	[11]
	390, 430	$(Mn^{2+})^*$	—	[10]
	465, 490, 530	$(Mn^{2+})^*$	—	[10, 11]

Thus, we arrive at the following mechanism of the observed phenomena: The dislocations that move under the influence of the external force stimulate a unique luminescence during the course of the plastic deformation. Under the influence of additional illumination, photobarriers are produced in the crystal and hinder the motion of the dislocations and lead to photohardening—the photoplastic effect. Accordingly, the strain-stimulated luminescence is likewise partly or completely suppressed under the influence of the light. Both the magnitude of the photoplastic effect and the effectiveness of the suppression of the luminescence N/N_L depend on the wavelength and intensity of the light and on the temperature. This is connected with the effectiveness of the formation and the charge transfer of the corresponding local centers which serve as photobarriers for the dislocations.

In conclusion, let us dwell on the minima in the plots of $N/N_L(\lambda)$ at the wavelength ~340 nm (see Figs. 2 and 4).

When the crystal is illuminated with light of $\lambda_{max} = 340$ nm, the number of luminescence flashes per unit time increases, i.e., the crystal becomes softer. The absorption coefficient of ZnS at 340 nm, in the investigated temperature region, is equal to several thousand cm^{-1}, meaning that the depth of penetration of light with wavelength 340 nm is equal to several microns. It is therefore more likely that the crystal becomes softer because the work of the surface-dislocation sources is facilitated by the illumination. Favoring this assumption is also the fact that the spectral characteristic of the softening is the same in crystals having different activators (ZnS:Cu and ZnS:Mn) (Figs. 2 and 4).

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[1] The ZnS:Mn samples were kindly supplied by A. I. Ryskin, to whom the authors are deeply grateful.

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