Charge exchange of hole centers in plastic deformation

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(Submitted October 7, 1976)
Pis'ma Zh. Eksp. Teor. Fiz. **24**, No. 9, 514–517 (5 November 1976)

Transport of holes from Tl^{++} to Cu^{+} ions by moving dislocations was observed in KCl:Cu:Tl crystals. This process changes the spectrum of the F-stimulated luminescence after plastic deformation of the sample.

PACS numbers: 78.60.Dg, 71.70.Ej

The deformation of colored alkali-halide crystals (AHC) with activators (Cu^{+}, Ag^{+}, Tl^{+}, ...) added leads to an increase of the activator glow stimulated by the F light.[1–3] This process, called strain sensitization, is of dislocation origin and proceeds in two stages. The dislocations that are set in motion by the deformation first capture holes (probably from optically inactive centers of unknown nature—X^{+} centers), and then transfer them (the holes) to Me^{+} centers. The concentration of the activator Me^{++} ions then increase, and this leads to the experimentally observed increase of the intensity of the luminescence stimulated by the F light, which is described by the scheme:

$$Me^{++} + e \rightarrow (Me^{+})^{*} \rightarrow Me^{+} + h\nu. \tag{1}$$

The electrons participating in the F-stimulated luminescence (FL) are released by the F light from the F centers. The first stage of strain sensitization in AHC + Me^{+} is a decrease in the number of X^{+} centers, and does not manifest itself optically, so that it could be discussed in[1,2] only hypothetically. We have succeeded in observing both stages of the strain sensitization. This was attained in the following manner.

According to the concepts developed in[1–3], the hole dislocation band D_p in KCl crystals lies in the forbidden band of the crystal above the levels of the Tl^{+} and In^{+} centers, but below the levels of the Cu^{+} and Ag^{+} ions. If this is correct, then by introducing into the crystal two activators (a_1 and a_2), the level of one of which lies above and the other below the hole dislocation band, one can expect the holes to be transported in the course of plastic deformation from the lower level a_1 to the upper a_2. This hole-transport process should manifest itself in a decrease of a_1 and an increase of a_2 bands in the spectrum of the F-stimulated luminescence. For a practical realization of such an experiment it is necessary also that the FL bands of the activators a_1 and a_2 not overlap. All these conditions are satisfied by KCl crystals doped with Tl^{+} and Cu^{+} ions.[1,2] An investigation of such samples, carried out in the present paper, has confirmed the foregoing assumptions. Following the deformation we observed a decrease in the number of Tl^{++} centers and an increase in the concentration of the Cu^{++} ions, a fact that manifested itself in the change of the intensities of the corresponding FL bands.

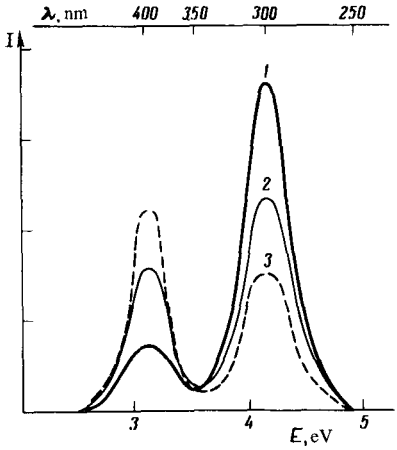

FIG. 1. Change of the spectrum of F-stimulated luminescence after plastic deformation: 1—undeformed crystal, 2—after 3% deformation, 3—after 8% deformation.

Quenched KCl samples containing Tl and Cu, measuring $3\times4\times10$ mm, were colored with a Co^{60} γ-ray source with a dose 10^6 rad at 300 °K, and then deformed at $T=100$—300 °K at a constant rate $\dot{\epsilon}=10^{-5}$ sec^{-1}. The concentrations of the Tl and Cu in the melt were varied in the range 3—5×10^{-2} at.%.[1)] The F-stimulated luminescence ($\lambda_{exc}=560$ nm) was registered with a large-aperture Hitachi monochromator and an FÉU-106 photomultiplier. The intensity of the F light was chosen such as to exclude a noticeable discoloring of the sample during the spectrum measurement.

Two bands were observed in the FL spectrum of the initial sample (Fig. 1)—short-wave ($\lambda=300$ nm) and long-wave ($\lambda=400$ nm). They coincide with the spectra of the intracenter luminescence of the activators Tl^+ and Cu^+, respectively,[4,5] meaning that they are described by the scheme (1). The plastic deformation leads to an appreciable change in the form of the spectrum: the intensity of the $\lambda=300$ nm band corresponding to the intracenter glow of Tl^+ decreases and long-wave intensity for which the Cu^+ centers are responsible increases. The evolution of the spectrum is monotonic and is practically completed at deformations $\sim 8\%$ (Fig. 2). The described process of the redistribution of the intensities of the FL bands in the system KCl : Cu : Tl is observed also in the case when the deformation is carried out at a temperature $T<300$K, in the entire investigated range $100\text{K}<T<300\text{K}$.

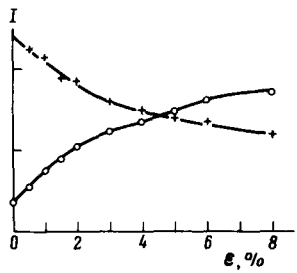

FIG. 2. Kinetics of variation of the intensities of the bands of the F-stimulated luminescence, corresponding to the luminescence of Tl^+ (crosses) and Cu^+ (circles) centers, as a function of the degree of deformation.

Variation of the ratio of the concentrations of the activators Tl and Cu in the indicated ranges leads to a change in the intensities of the corresponding bands in the *FL* spectrum of the initial sample. The main features of the transformation of the spectrum under plastic deformation (the decrease of the 300 mm band and the increase of the luminescence with $\lambda = 400$ nm) remain the same, however.

To establish the laws governing the redistribution of the holes among the Tl and Cu ions in the deformed crystals, we determined the relative number of Tl^{++} and Cu^{++} centers in the initial crystal (n_{Tl} and n_{Cu}) and in the identical deformed crystal (n^*_{Tl}, n^*_{Cu}); the concentrations of the Tl^{++} and Cu^{++} ions were obtained by the method described in[1] from the number of light quanta with $\lambda = 300$ nm and $\lambda = 400$ nm, emitted upon discoloration of the crystal.

For all the samples investigated in the present study, the concentration of the Tl^{++} centers decreases and that of the Cu^{++} ions increase after plastic deformation. The ratio of the number of Cu^{++} centers produced by a deformation $\Delta n_{Cu} = n^*_{Cu} - n_{Cu}$ and the annihilated Tl^{++} ions $\Delta n_{Tl} = n_{Tl} - n^*_{Tl}$ varies between $\Delta n_{Tl} = 0.7\,\Delta n_{Cu}$ and $\Delta n_{Tl} \approx \Delta n_{Cu}$. At $\Delta n_{Tl} \approx \Delta n_{Cu}$, the X^+ centers do not take part in the strain sensitization process and the holes are transported by the dislocations from the Tl^{++} to the Cu^+ centers.

The independence of the strain sensitization of the temperature in KCl: Tl: Cu crystals allows us to conclude that the first and second stages of the process require no temperature activation, i.e., during each stage of the strain sensitization the holes "float up" in the forbidden band. This means that in KCl: Tl: Cu crystals, just as in KCl: Me^+, the moving dislocations capture into the hole dislocation band the holes that are localized in shallower traps (Tl^+ or *X* centers). The holes captured by the dislocation (just as the electrons in the electron dislocation band[6]) can participate in two motions. They move along the dislocation because the latter is one-dimensional, and move over the crystal with the moving dislocation. These quasi-free holes are captured by the Me^+ centers, the levels of which lie in the forbidden band above the hole dislocation band. The results obtained in the present paper offer evidence also that the concepts introduced in[1-3], concerning the hole dislocation band and the data on its position in the band scheme of the crystal are indeed correct.

We are grateful to V. L. Broude for useful discussions.

[1)]The crystals were grown by V. N. Erofeev and Z. Ivanova, to whom the authors are deeply grateful.

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