Deformation-stimulated emission of ZnS crystals

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Emission of short light pulses following deformation of ZnS crystals has been observed. The spectral, temporal, and temperature characteristics of the process were investigated. It is shown that the emission is produced by a dislocation mechanism.

It was shown in[1-3] that dislocations moving under the influence of a mechanical stress in colored alkali-halide crystals produce a glow (deformation luminescence). In the case of plastic deformation, the deformation luminescence in these crystals is stationary. Emission of a different character, mainly in the form of short light pulses, was observed in the present study following plastic deformation of ZnS crystals.

The investigations were performed with ZnS crystals grown from the melt by the Bridgman method at 600 atm pressure in an atmosphere of argon.1) The crystals, with dimensions 2×2×4 mm, a faceting (1$\bar{2}$10) and (10$\bar{1}$1), the basal plane making an angle of 45° to the deforming stress. The deformation was produced with an electromagnetic setup described in[2]. The crystal temperature was maintained accurate to ±0.5°. The luminescence was registered with FEU-77 photomultipliers and with an S1-37 or S1-11 oscilloscope. The procedure used for the spectral investigations is described in[2]. To exclude possible storage of the light sum, the samples were heated prior to the investigation at 500 °C for 20 minutes in a lightproof thermostat, in which the experiments were subsequently carried out.

The crystal was loaded with square mechanical stress pulses of duration 0.2–30 sec. In the elastic deformation region, no luminescence was observed. At stresses $\sigma \sim \sigma_{el}$ (σ_{el} is the elastic limit), individual light flashes are produced (Fig. 1). The number of flashes per unit time (N) increases with increasing external stress (Fig. 1). The luminescence vanishes when the crystal stress is relieved. An increase of the temperature at a fixed value of σ also leads to an increase of N (Fig. 2). The value of N increases 30 times when the crystal is heated from 62 to 96 °C. The parameters (amplitude and duration) of an individual light flash depend little on the external stress and on the temperature at which the sample is stressed. At the same time, the duration of the light pulse τ decreases with increasing degree of deformation of the crystal. In the initial samples we had $\tau_{0.5} \sim 0.2$ μsec, and after a 3% deformation $\tau_{0.5} \sim 0.05$ μsec.

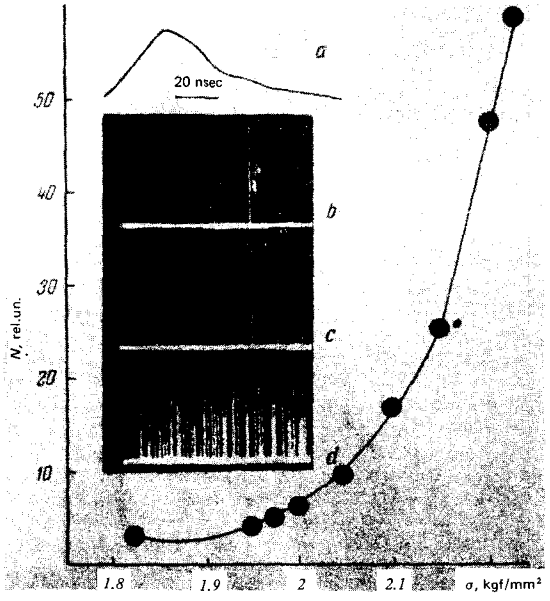

FIG. 1. Dependence of the number of luminescence flashes (N) on the external stress (σ). (The shown values of N are averages of 10 measurements): a—waveform of the luminescence pulse, b,c,d—oscillograms of the luminescence at different values of σ ($T = 80°$); scale: 1 cm = 250 msec.

The emission spectrum has a principal maximum at $E \sim 3.56$ eV and steps at 3.30 and 3.10 eV. A similar luminescence spectrum was observed when the crystal was excited with light with $E = E_g$ (E_g is the width of the forbidden band). According to the published data, the luminescence bands observed by us are connected with the presence of oxygen as an impurity in the ZnS samples.[4]

Examination of the crystal between crossed polarization prisms has shown that a slip band appears in synchronism with the luminescence flash. Since the slip band is produced by moving dislocations, it can be assumed that the luminescence flashes are of dislocation origin.

Figure 3 shows the residual deformation on the crystal (ϵ), produced after the emission of different numbers of luminescence flashes at equal stress durations. It is seen from Fig. 3 that the residual deformation is pro-

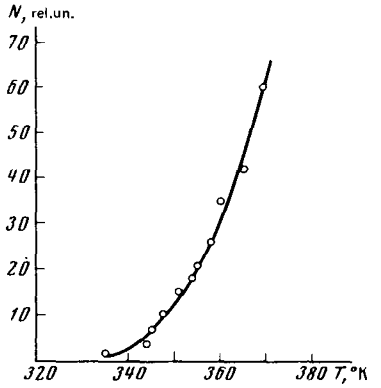

FIG. 2. Dependence of the number of luminescence flashes (N) on the temperature.

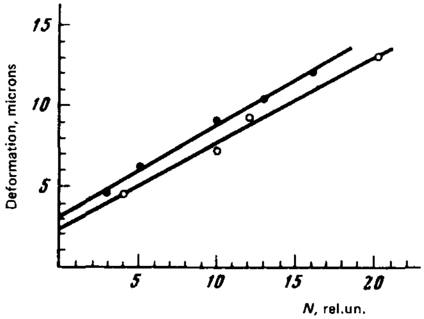

FIG. 3. Dependence of the residual deformation in the crystal (ϵ) on the number of luminescence flashes (N). ● — $T = 100$°C, ○ — $T = 80$°C.

portional to the number of luminescence flashes, and the deformation per flash depends little on T. These experiments lead to the following conclusions: 1) The luminescence flashes are the result of plastic deformation of the sample, which in turn is the consequence of motion and multiplication of the dislocations. 2) In the investigated crystals, the deformation is produced jumpwise and a certain delay time, which depends on σ and T, is needed to produce the deformation (Fig. 1).

The maximum residual deformation produced when one dislocation passes through the sample is ~a (a is the lattice constant). The deformation corresponding to one luminescence flash is ~0.5 μ. This means that each luminescence flash is produced by a large number of dislocations which, as follows from polarization investigations, indeed form the slip bands.

If it is assumed that the luminescence flashes are produced by a dislocation mechanism, then we can expect the flashes to become weaker or to vanish under conditions when the motion and multiplication of the dislocations is hindered. Indeed, the deformation of a crystal cut in such a way that the basal plane was parallel to the deformation direction did not lead (even at $T = 150$°C) to the appearance of luminescence flashes, up to when the deformation reached the failure point.

Other nondislocation mechanisms producing the luminescence flashes can not explain the number of experimental facts. The piezofield produced when the crystal is loaded can cause electro-luminescence. However, the piezoeffect does not explain the discrete character of the luminescence, its dependence on σ and T, and the absence of luminescence flashes when the crystal is loaded parallel to the basal plane.

The luminescence investigated by us is not triboluminescence, or the luminescence produced in a crystal by friction. Observation of the luminescence with an electron-optical converter has shown that in a number of cases the entire basal plane glows. The onset of such a crack would lead to breakdown of the sample. At the same time, it is easy to deform the crystal by 25%, and such a deformation is companied by several thousand luminescence flashes, but observation with an optical microscope does not show any continuity disturbances in the deformed sample. In addition, according to[5], triboluminescence decreases strongly with decreasing temperature at which the crystal is deformed. This contradicts our results.

Thus, it seems to us that we have proved the dislocation mechanism of luminescence flashes in deformed ZnS crystals. On the other hand, the luminescence of a number of crystals (NaCl : Mn, ZnS : Mn, etc.), observed in[6], is apparently triboluminescence.

We note in conclusion that stressing ZnS crystals also produces luminescence, but in these samples the observed luminescence is stationary and the glow is produced during the entire time of loading.

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