Interaction of dislocations with hole centers in colored alkali-halid crystals

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(Submitted June 18, 1973)
Zh. Eksp. Teor. Fiz. 65, 2356–2363 (December, 1973)

Transport of holes by moving dislocations towards the activator ions (Cu^+) with formation of Cu^{++} centers, the so-called deformation sensitization, is observed in colored alkali-halide crystals. The spectral, kinetic, and temperature characteristics of the process are investigated. A mechanism is proposed for this process. The kinetic equations describing the deformation sensitization are solved. The quantities characterizing the interaction of the dislocations with the hole centers are obtained.

An investigation of the influence of deformation on colored alkali-halide crystals has shown that the dislocations that move when the crystal is loaded change the distribution of the electron and hole centers[1,2]. We investigated the interaction of dislocations with electron centers in detail earlier[2-5]. We have shown that the moving dislocations destroy the F centers. Recombination of the F-electron centers released by the dislocations with the holes localized on the luminescence centers leads to emission of light (deformation luminescence). An analysis of the temporal and temperature characteristics of the luminescence has made it possible to demonstrate the existence of a bound state of electrons on dislocations and to determine the position of the dislocation subband in the band scheme of the crystal.

Additional information on the energy characteristics of the dislocations can be obtained by investigating the interaction of dislocations with hole centers; such an investigation is described in this paper. It turns out that plastic deformation of colored KCl : Cu crystals leads to an appreciable increase of the Cu^{++}-center concentration (deformation sensitization). We investigated the kinetics of the growth of the number of Cu^{++} centers in the course of the deformation of the crystal at different temperatures, as well as their spectral characteristics. A mechanism of deformation sensitization is proposed.

EXPERIMENTAL PROCEDURE

The objects of the investigation were hardened KCl single crystals doped with copper to a concentration 4×10^{-4} mol%. The crystals were exposed at T = 300°K to γ radiation from Co^{60}, the irradiation dose being $(0.2-1) \times 10^6$ rad. The spectral investigations were performed with the setup illustrated in Fig. 1. The light source was either an SI-8-200u ribbon-type incandescent lamp or a xenon lamp. Special measures were taken to maintain the light flux constant. The radiation receivers were FÉU-79 photomultipliers. The photomultipliers 6, 10, and 8 were used to investigate the absorption spectra and the luminescence spectra of the sample, and to count the number of light quanta emitted by the crystal.

The sample was placed in a straining device that made it possible to deform the crystal at different rates: 10, 50, 100, and 500 μ/min. The samples were cooled from 300 to 77°K in a special cryostat. The crystal temperature was maintained accurate to ±0.5°.

The experimental procedure consisted in the following. The sample irradiated at room temperature was placed in the straining device and was cooled to the corresponding temperature, at which all the measurements were then carried out.

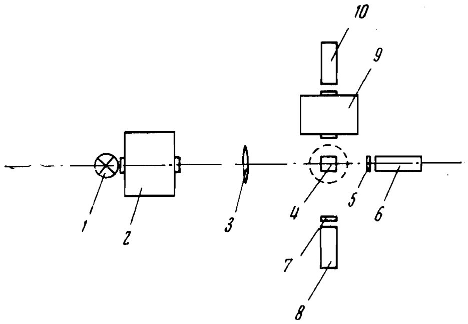

FIG. 1. Diagram of experimental setup: 1—light source; 2—SPM-2 monochromator; 3—lens system; 4—investigated sample in straining machine; 5, 7—optical interference filters with λ_{max} = 560 nm and λ_{max} = 400 nm; 6, 8, 10—FEU-79 photomultipliers, 9—Hitachi monochromator.

EXPERIMENTAL RESULTS

Illumination of a colored crystal by light corresponding to the maximum F-center absorption (λ = 560 nm) leads to the appearance of activator luminescence (Fig. 2). The luminescence band with λ_{max} = 400 nm is the intracenter luminescence of the Cu^+ center[6], which appears when the electron released by the F-illumination recombines with a hole localized on a Cu^+ center:

$$Cu^{++}+e \rightarrow (Cu^+)^* \rightarrow Cu^+ + h\nu.$$

Luminescence with λ_{max} equal to 450 and 490 nm corresponds to the luminescence of the more complicated Cu^+ centers near O_2[7] and to a complex of Cu^+ centers[8]. Plastic deformation of the crystal in the temperature interval 300–77°K leads to an appreciable change of the form of the spectrum of the F-stimulated luminescence. The intensity of the short-wave band increases appreciably. At the same time, the long-wave bands remain practically unchanged (see Fig. 2).

It is easy to show that at

$$\omega_c n_c \ll \omega_a n_a, \tag{1}$$

where n_c and n_a are the numbers of the Cu^{++} centers and of all the hole centers other than Cu^{++}, while ω_c and ω_a are the probabilities of electron capture by these centers, the intensity of the F-stimulated luminescence with λ_{max} = 400 nm is equal to

$$I = A\eta n_c,$$

where A is a constant proportional to the intensity of the F-light and η is the quantum yield of the intracenter luminescence with λ_{max} = 400 nm.

Relation (1) is probably satisfied in our case, inasmuch as $n_c \ll n_a$ (this is demonstrated below), and at the same time the intensities of the luminescence bands with λ_{max} equal to 450 and 490 nm (prior to deformation) are comparable with the luminescence intensity of the Cu^+ centers. This means that the increase of the F-stimulated luminescence is due to the growth of the number of Cu^{++} centers, with I proportional to n_c.

The increase in the number of Cu^{++} centers in the course of plastic deformation at different temperatures is shown in Fig. 3. We see that the general character of this dependence is the same at different temperatures. We first have an intense growth of the number of Cu^{++} centers with increasing ϵ, and then saturation sets in at a deformation ~3–4%. Illumination of the deformed crystal by F light leads to an exponential decrease of the number of Cu^{++} centers. Subsequent deformation is again accompanied by an increase of the intensity of the band with λ_{max} = 400 nm to its previous value, see Fig. 3. The described regularities were observed at all the investigated temperatures.

We have determined the number of Cu^{++} centers produced as a result of the deformation of the crystal at different temperatures. The investigated sample was deformed at the corresponding temperature until the deformation sensitization exhibited saturation. The crystal was then illuminated with F light until the intensity of the luminescence with λ_{max} = 400 nm reached the initial value (prior to the deformation of the sample). At the same time, we registered the number N_0 of the light quanta emitted in the course of discoloration at λ_{max} = 400 nm. It is clear that the number of Cu^{++} centers produced upon deformation is $N = N_0\eta^{-1}$. The quantity η is equal to the quantum yield η_F of the F-stimulated luminescence at a large activator concentration, when all the holes produced by γ-irradiation are captured by the Cu^{++} centers. By definition we have

$$\eta_F = n_0/\Delta N_F,$$

where $\Delta N_F = N_1 - N_2$ is the number of F centers annihilated upon illumination of the colored crystal, n_0 is the number of light quanta with λ_{max} = 400 nm emitted in this case, and N_1 and N_2 are the numbers of F centers before and after illumination. The number of color centers was determined from the contour of the F absorption band using Smakula's formula. The value of n_0 was determined by a method described earlier[2]. The value of η was[1)] ~ 10^{-2}.

When a colored crystal is deformed, a certain number (ΔN) of Cu^{++} centers is annihilated as a result of recombination with the electrons released by the dislocations (deformation luminescence). The intensity of the deformation luminescence decreases rapidly with decreasing temperature, and since $\Delta N \ll N$ in the crystals investigated by us even at room temperature, there is no need to take ΔN into account. The numbers of the Cu^{++} centers produced as a result of the deformation at 300, 200, 180, and 110°K are respectively 1.45×10^{15}, 1.16×10^{15}, 1.7×10^{15}, and 1.45×10^{15} cm^{-3}. The accuracy with which N is determined is 25%. This means that N is independent of the temperature within the limits of experimental error. A study of the deformation-sensitization effect at different deformation rates ($\dot{\epsilon}$ ranged from 3×10^{-5} to 10^{-3} sec^{-1}) has shown that N does not depend on the rate of deformation of the sample.

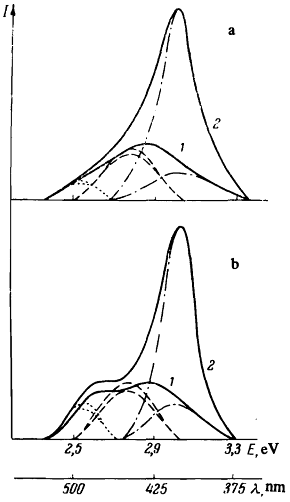

FIG. 2

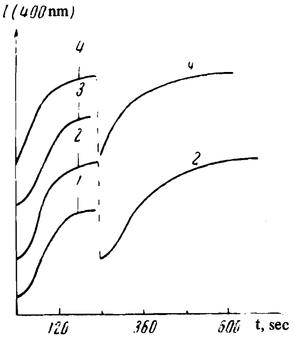

FIG. 3

FIG. 2. Spectra of F-stimulated luminescence of KCl crystals + 4×10^{-4} mol. % Cu: 1–initial sample; 2–sample subjected to plastic deformation; remaining lines–resolution of spectra into components: a–at T = 300°K; b–at T = 110°K.

FIG. 3. Dependence of the deformation sensitization on the deformation time (deformation rate $\dot{\epsilon} = 10^{-4}$ sec^{-1}) at different temperatures: 1–T = 130°K, 2–T = 150°K, 3–T = 200°K, 4–T = 300°K. Curves 2 and 4 were obtained after 3.2% deformation of the crystal, continuous illumination with F light, and further deformation.

DISCUSSION OF EXPERIMENTAL RESULTS

An increase of the concentration of the Cu^{++} centers in colored crystals occurs upon plastic deformation which, in turn, is the result of motion and multiplication of dislocations. This means that deformation sensitization is either a dynamic effect, i.e., the result of dislocation motion, or is connected with the presence in the crystal of a large concentration of dislocations produced as a result of the deformation.

The following experiment enables us to choose one of the alternatives. One of two identical samples was deformed plastically (ϵ ~ 4%), after which both samples were colored. A comparison of the spectra of the F-stimulated luminescence of the crystal deformed prior to coloring with the nondeformed crystal has shown that the two spectra coincide. Thus, the presence of a large dislocation concentration alone does not increase the concentration of the Cu^{++} centers.

Thus, deformation sensitization is the result of transport of the holes by the moving dislocations towards the Cu^+ centers.

The luminescence centers that become optically manifest in F-stimulated luminescence (λ_{max} equal to 450 and 490 nm) do not supply holes during the course of the deformation sensitization, since these centers are not destroyed by the deformation of the crystal (Fig. 2). It remains therefore to assume that optically inactive X^+ centers take part in the deformation sensitization. The structure of the X^+ centers is not known, but it is most probably a series of levels by which the hole is captured when the crystal is irradiated.

The migration of the holes to the Cu^+ centers can be effected either through the valence band or because the holes, like the electrons, are captured in the hole dislocation band and are supplied to the Cu^+ centers by the moving dislocations. If it is assumed that the holes are supplied to the Cu$^+$ ions via the valence band, then the number of Cu^{++} ions produced during the course of the deformation should decrease sharply at T < 210°K, inasmuch as at these temperatures the holes in the KCl lose their mobility and are autolocalized[9]. This conclusion contradicts the experimental results. It means that we are left with the second method of hole transport to the Cu$^+$ centers, through the dislocation band. The absence of temperature activation in the process of deformation sensitization is evidence that the hole dislocation band is located in the forbidden band between the levels of the X$^+$ and Cu$^+$ centers, i.e., at a distance shorter than 2.5 eV from the valence band[10].

It follows from the foregoing that the dislocations moving under the influence of the external stress capture holes localized on X$^+$ centers and transport them to the Cu$^+$ centers. Now that the mechanism whereby the holes are transported by the dislocations to the Cu$^+$ centers is known, we can write down for the process the kinetic equations whose solution will make it possible to determine the parameters of the dislocation interaction with the X$^+$ and Cu$^+$ centers.

KINETIC EQUATIONS OF THE DEFORMATION SENSITIZATION PROCESS

We introduce the following notation: n_F is the number of F centers; n is the number of X$^+$ centers; $n^0 = n(t = 0)$; n_d is the number of holes at the dislocations; $\tilde{n}_d^0 = n_d(t = t_{sat})$; t_{sat} is the time at which the number of Cu^{++} centers reaches saturation; n_d^0 is the number of points at which the holes can land on the dislocations; n_c is the number of Cu^{++} centers; $n_c^0 = n_c(t = 0)$; $N = n_c(t = t_{sat})$; ω_F, ω, and ω_d are constants characterizing the interaction of the dislocations with the F, X$^+$, and Cu$^+$ centers. The kinetic equations describing the process of hole transport by the dislocations can then be expressed in the form

$$\dot{n} = -\omega(n_d{}^0 - n_d)n, \tag{2}$$

$$\dot{n}_d = \omega(n_d{}^0 - n_d)n - \omega_d n_d(N - n_c) - \omega_F n_F n_d, \tag{3}$$

$$\dot{n}_c = \omega_d n_d (N - n_c). \tag{4}$$

This nonlinear system of equations has no analytic solution. It was solved approximately using the above-described experimental data.

It was shown that repeated deformation of a previously deformed and illuminated crystal leads to an increase in the concentration of the Cu^{++} centers back to the value N (Fig. 3). This experiment offers evidence that the number of X$^+$ centers remains practically unchanged (accurate to 10%) when the crystal is loaded until the deformation sensitization is saturated. Taking the constancy of the number of X$^+$ centers into account, let us examine the solution of the system in limiting cases.

1. $n_d \ll n_d^0$, $n_c \ll N$. From (3) and (4) we have

$$n_c = {}^1/{}_2\,\omega n_d{}^0 \omega_d N n^0 t^2 + n_c{}^0, \qquad n_d = \omega n_d{}^0 n^0 t.$$

This case is obtained when $t < (\omega_d N + \omega_F n_F)^{-1}$.

2. $n_c \ll N$. When $t > (\omega n^0 + \omega_F n_F + \omega_d N)^{-1}$ we have

$$n_d = \frac{\omega n^0 n_d{}^0}{\omega n^0 + \omega_F n_F + \omega_d N} = n_d{}^1$$

Then

$$n_c = N - (N - n_c{}^0)\exp(-\omega_d n_d{}^1 t). \tag{5}$$

We see that this condition is valid when $t < (\omega_d n_d^1)^{-1}$.

3. $n_c \sim N$. By solving (3) and (4) we easily obtain

$$n_c = N - (N - n_c{}^0)\exp(-\omega_d \tilde{n}_d{}^0 t), \qquad n_d = \frac{\omega n^0 n_d{}^0}{\omega n^0 + \omega_F n_F} = \tilde{n}_d{}^0. \tag{6}$$

Therefore $n_c \sim N$ at $t > (\omega n^0 + \omega_F n_F)/\omega_d n_d^0 \omega n^0$.

Thus, at $t < (\omega_d N + \omega_F n_F)^{-1}$ the number of Cu^{++} centers increases quadratically with time; at

$$\frac{1}{\omega n^0 + \omega_F n_F + \omega_d N} < t < \frac{\omega n^0 + \omega_F n_F + \omega_d N}{\omega_d n_d{}^0 \omega n^0}$$

the quantity $N - n_c$ varies exponentially with time; finally, at $t > (\omega n^0 + \omega_F n_F)/\omega_d n_d^0 \omega n^0$ the difference $N - n_c$ has likewise an exponential dependence on t. The arguments of the exponentials are different in the last two cases.

Figure 4 shows the experimentally obtained plots of $\ln(N - n_c) = f(t)$. We see that there exist three regions of t in which the character of the behavior of $\ln(N - n_c)$ is different. In region 1 (small t), this function changes little with time, after which an exponential decrease of $N - n_c$ sets in (region 2). This exponential then gives way to an exponential with a larger argument in region 3. With decreasing temperature, the length of the initial section increases somewhat. Comparing calculation and experiment, we reach the conclusion that they are in qualitative agreement. This is an additional confirmation of the validity of the previously described deformation-sensitization mechanism.

The quantities characterizing the interaction of the dislocations with the X$^+$ and Cu$^+$ centers can easily be obtained from (5) and (6):

$$\omega_d = \frac{|\operatorname{tg}\varphi_2|(\omega n^0 + \omega_F n_F)}{\omega n^0 n_d{}^0}, \tag{7}$$

$$\omega = \frac{N}{n^0 n_d{}^0}\,\frac{\operatorname{tg}\varphi_1 \operatorname{tg}\varphi_2}{|\operatorname{tg}\varphi_2| - |\operatorname{tg}\varphi_1|}, \tag{8}$$

where $\tan\varphi_1$ and $\tan\varphi_2$ are the slopes of the plots of $\ln(N - n_c) = f(t)$, with $|\tan\varphi_1| < |\tan\varphi_2|$. The values of $\tan\varphi_1$, $\tan\varphi_2$ and N, as noted above, were obtained experimentally. The determination of n^0, n_d^0, and ω_F entails great experimental difficulties, and only the orders of magnitude of these quantities can be obtained at present.

The quantity n^0 should be larger by at least one order of magnitude than N ($N \sim 10^{15}$ cm^{-3}), since repeated deformation after prior emission of the band with $\lambda_{max} = 400$ nm leads to generation of N Cu$^+$ centers, i.e., $n^0 \sim 10^{16}$ cm^{-3}. On the other hand, the total number of holes produced by the irradiation is equal to the number of generated F centers, $n_F = 3 \times 10^{15}$ cm^{-3}, and this is

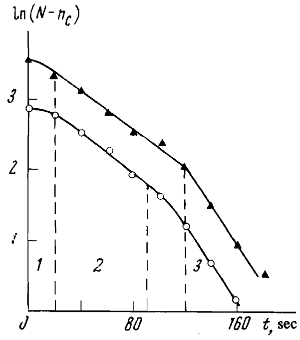

FIG. 4. Plot of $\ln(N - n_c)$ against the deformation time for a KCl + 4 × 10^{-4} mol. % Cu crystal at T = 150°K (▲) and T = 300°K (○). The deformation rate is $\dot{\epsilon} = 10^{-4}$ sec^{-1}.

the upper estimated limit of n^0. This means that $10^{16}\ \mathrm{cm}^{-3} < n^0 < 3 \times 10^{16}\ \mathrm{cm}^{-3}$. Assuming the dislocation density in the crystal at $\epsilon = 3\%$ to be of the order of $10^7\ \mathrm{cm}^{-3}$, we obtain $n_d^0 = 3 \times 10^{14}\ \mathrm{cm}^{-3}$.

As already noted, when the crystal is loaded for a time $t = t_{sat}$, the number of X^+ centers decreases by less than 10%, so that it follows from (2) that

$$\omega (n_d{}^0 - \tilde{n}_d{}^0)\, n^0 \leqslant 0.1 n^0 / t_{\mathrm{sat}}. \tag{9}$$

Since $\dot{n}_d(t \to t_{sat}) \to 0$, we obtain from (3) and (9)

$$\frac{\omega n^0 n_d{}^0 \omega_F n_F}{\omega n^0 + \omega_F n_F} \leqslant \frac{0.1 n^0}{t_{\mathrm{sat}}}. \tag{10}$$

At $n_d^0 = 3 \times 10^4$ and $n^0 = 2 \times 10^{16}\ \mathrm{cm}^{-3}$ it follows from (7), (8), and (10) that

$$\omega_d = 1.4 \cdot 10^{-16}\ \mathrm{cm}^3 \cdot \mathrm{sec}^{-1}, \qquad \omega = 5 \cdot 10^{-18}\ \mathrm{cm}^3 \cdot \mathrm{sec}^{-1}, \quad \omega_F = 1.6 \cdot 10^{-18}\ \mathrm{cm}^3 \cdot \mathrm{sec}^{-1}.$$

An estimate of the values of ω_d, ω, and ω_F can be obtained from the values of t at which the character of the $\ln (N - n_c) = f(t)$ dependence changes. Assuming

$$\frac{\omega n^0 + \omega_F n_F}{\omega_d n_d{}^0 \omega n^0} = 90\ \mathrm{sec}, \quad \frac{\omega n^0 + \omega_F n_F + \omega_d N}{\omega_d n_d{}^0 \omega n^0} = 120\ \mathrm{sec}$$

and using relation (9), we obtain $\omega_d = 7 \times 10^{-17}\ \mathrm{cm}^3\,\mathrm{sec}^{-1}$, $\omega = 7 \times 10^{-18}\ \mathrm{cm}^3\,\mathrm{sec}^{-1}$, and $\omega_F = 1.8 \times 10^{-18}\ \mathrm{cm}^3\,\mathrm{sec}^{-1}$. We see that they are close to the previously determined values of ω, ω_d, and ω_F.

The radius of discoloration of F centers by dislocations was determined earlier in[2]. We deemed it advisable to determine the analogous quantity r_d from the interaction between the dislocations and the X^+ centers. The rate of destruction of the X^+ centers upon deformation is

$$\dot{n} = n \dot{S} r_d / V_0, \tag{11}$$

where V_0 is the volume of the crystal and S is the area traversed by the dislocations. By definition, $\dot{S} = 2\dot{\epsilon} V_0 / b$, where b is the Burgers vector. From (11) and (2), and (8) we obtain

$$r_d = \frac{N (n_d{}^0 - n_d)}{2 \dot{\varepsilon} n^0 n_d{}^0} \frac{\mathrm{tg}\, \varphi_1\, \mathrm{tg}\, \varphi_2}{|\mathrm{tg}\, \varphi_2| - |\mathrm{tg}\, \varphi_1|} b.$$

It follows from this relation that r_d changes with increasing degree of deformation from $r_{d\,\max} \sim 7b$ to $r_{d\,\min} \sim 2.5b$. The value of $r_{d\,\max}$ for the investigated crystals exceeds the cross section for the dislocation of F centers by almost one order of magnitude.

We are grateful to V. L. Broude and G. I. Babkin for valuable advice and remarks.

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1)The value of $\eta = \eta_F$ was determined in KCl + 5 × 10^{-3} % Cu crystals.

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Translated by J. G. Adashko
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