Kinetics of photostimulated change of dislocation charge in NaCl crystals

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The kinetics of the photostimulated change of the electric charge on dislocations in NaCl single crystals in which color centers (*F* centers) are introduced is investigated in detail as a function of the intensity and the duration of the illumination in the temperature interval 220–320 K. It is observed that the photostimulated change of the dislocation charge has a complicated and nonmonotonic character, and under certain conditions the sign of the charge can be reversed. The observed change of the charge can be described by a 3-stage process. The empirical relations that describe each of the stages are found, and their main characteristics are studied. A model is proposed, according to which the photostimulated change of the dislocation charge is connected with the capture of photoelectrons and anion vacancies, which are produced when the *F* centers are photoionized, followed by a redistribution of the cation and anion vacancies between the dislocation, the screening charge cloud, and the bulk of the crystal. The theoretical relations for the kinetics of photostimulated charge change agree well with the experimental results.

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The charges on dislocations in alkali-halide crystals (AHC) and their influence on the physical properties of these crystals have been intensively investigated in the last few years.[1-4] Of great interest is the study of the dislocation charge in AHC in which electronic color centers (usually *F* centers) have been introduced. In such crystals the photoionization of the *F* centers leads to slowing down of the dislocations (the photoplastic effect) and to a temporal redistribution of the carriers responsible for the formation of the dislocation charge. This manifests itself in an effect recently observed in NaCl crystals, namely *F*-stimulated reversal of the sign of the charge on the dislocation.[2] Understandably, the two effects are related and therefore an understanding of the nature of one of them yields essential information for the understanding of the other. The present paper is devoted to an investigation of the kinetics of the photostimulated change of the dislocation charge in NaCl crystals.

EXPERIMENTAL PROCEDURE

To measure the dislocation charge we used a 4-component piezoelectric vibrator (Fig. 1). The method is based on the known fact[3] that if longitudinal mechanical vibrations are excited in a sample subjected to prior deformation by flexure, an alternating voltage U appears between its opposite faces on account of the periodic displacements of the charged dislocations (see the right-hand part of Fig. 1). The connection between U and the charge on the dislocation is established in the following manner. The displacement of the dislocation under the influence of the applied stress causes a dislocation strain $\varepsilon_{\rm disl}=N_1 b\bar{\xi}_1$, where N_1 is the density of the mobile dislocations, b is the Burgers vector, and $\bar{\xi}_1$ is the average displacement of the dislocations. In addition, displacements of the charged dislocations lead to sample polarization $P=qN_2\bar{\xi}_2$, where q is the linear charge of the dislocation, N_2 is the density of the excess edge dislocations that are produced by the bending of the sample, and $\bar{\xi}_2$ is the average displacement of the dislocation relative to its screening charge cloud.

As shown by Robinson *et al.*,[4] the charge cloud is immobile up to temperatures ~600 K, so that in our case $\bar{\xi}_1=\bar{\xi}_2$, inasmuch as the employed temperatures were substantially lowered in 600 K. Thus, the alternating voltage U produced by displacement of the dislocations can be expressed in terms of the parameters of the dislocation structure: $U=\alpha_1 qN_2\bar{\xi}_2$, where α_1 is a coefficient that takes into account the electrical characteristics of the measuring circuit. Expressing $\bar{\xi}_2$ in terms of $\bar{\xi}_1$, we obtain ultimately

$$U=\alpha_1\frac{N_2}{N_1}\frac{q}{b}\varepsilon_{\rm disl}. \tag{1}$$

As seen from (1), the quantities α_1 and N_2/N_1 are constants for a given sample and for a chosen measurement setup, therefore to estimate q it is necessary to determine U and $\varepsilon_{\rm disl}$ from experiment. The alternating voltage U is obtained from direct measurements of the potential difference between the faces of the sample, and $\varepsilon_{\rm disl}$ is determined from the measured amplitude-dependent decrement δ

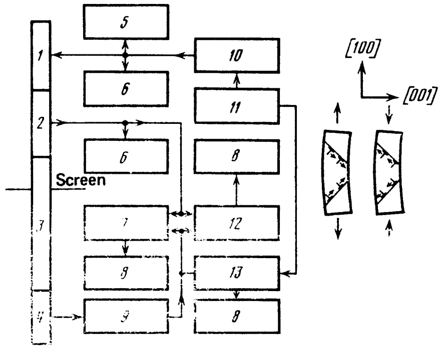

FIG. 1. Block diagram of the setup: 1—quartz exciter, 2—quartz receiver, 3—fused-quartz buffer, 4—sample, 5—frequency meter, 6—voltmeter, 7—phase meter, 8—automatic plotter, 9—narrow-band amplifier, 10—amplifier, 11—sweep generator, 12—current-frequency characteristics meter, 13—synchronous detector. On the right is shown the pattern of motion of the excess edge dislocations in a bent sample under the influence of compression and tension stresses.

and the change of the elastic modulus $\Delta\mu/\mu$.

Within the framework of the string model[5] for this procedure all these quantities are connected by the simple relation

$$\varepsilon_{\text{disl}}=\delta\varepsilon_0=2(\Delta\mu/\mu)\varepsilon_0,$$

where ε_0 is the amplitude of the mechanical stress applied to the sample.

The measurement circuit is shown in Fig. 1. A voltage v_t is applied to the quartz exciter from a generator. As a result, natural longitudinal oscillations are excited in the vibrator, which consists of the quartz exciter, quartz receiver, buffer, and sample.

The amplitudes v_d of these vibrations are registered by the quartz receiver. The alternating voltage U, which is produced only when an excess density of edge dislocations is introduced into the sample by flexure, is picked off simultaneously from the silver-coated faces of the sample. The voltage U is applied through an amplifier to a measuring instrument and a synchronous detector. The amplitude- and phase-frequency characteristics of the voltage U and of the voltage from the quartz receiver are recorded with automatic plotters. To eliminate electric noise, a buffer of fused quartz and a brass screen are placed between the sample and the quartz crystals. For the same reason, the entire vibrator is placed in a metallic vessel.

The quantities δ, ε_0, and $\Delta\mu/\mu$ can be expressed, within the framework of the theory of the compound piezoelectric vibrator,[6] in terms of measurable parameters of the electric circuit: $\varepsilon_0=k_1v_d$, $\delta=k_2v_t/v_d$, $\Delta\mu/\mu=k_3\Delta f$, where Δf is the change of the resonant frequency of the vibrator, measured with a frequency meter, and k_1, k_2, and k_3 are the characteristic parameters of the circuit. Thus, expression (1) can be represented in terms of the measured parameters of the electric circuit of the vibrator:

$$U=\alpha_1\frac{N_2}{N_1}\frac{q}{b}k_2\frac{v_{\text{t}}}{v_{\text{d}}}k_1v_{\text{d}}=\alpha_1k_1k_2\frac{N_2}{N_1}\frac{q}{b}v_{\text{t}}. \tag{2}$$

It should be noted that, as seen from (2), $q\sim U$ when v_t is constant.

The employed measurement circuit makes it possible not only to estimate the absolute value of the charge, but also to determine its sign. To this end, the sign of the piezoelectric modulus for the chosen face is first determined from static experiments on the quartz receiver. This makes it possible to ascertain, from the voltage v_d picked off the quartz receiver in the dynamic regime, whether the positive (negative) half-wave of the picked-off voltage belongs to the compression or tension cycle. Knowing the distribution of the stresses in the vibrator at each instant of time, we can determine for the second instant of time the distribution of the stresses in the sample. Since the slip geometry in the sample is known (see Fig. 1), the sign of q can be determined by measuring the phase relations between U and v_d.

The experiment was performed in the following manner. Samples measuring 3×3×21 mm were cleaved along the [100] planes from single crystals of NaCl containing $<10^{-3}$ at.% impurities. Measures were taken in the course of the preparation of the samples[7] to prevent a possible increase of the dislocation density when the samples are attuned to the required frequency (~100 kHz). Silver electrodes were coated on the prepared samples, after which the samples were bombarded with gamma rays up to a dose of 1×10^6 rad, corresponding to introduction of $\sim10^{16}$ cm^{-3} F centers. The samples with the introduced color centers were then deformed in darkness by 4-point bending to a radius ~0.7 m. According to Whitworth,[8] this corresponds to introduction of an excess of $\sim10^6$ cm^{-2} edge dislocations. The measurements were made in the temperature 220–320 K, but at fixed temperatures. The sample was kept at the specified temperature prior to the start of the experiment for a time not less than 30 min. The rate of heating or cooling on going from one temperature to the other did not exceed 1 K/min. In the entire temperature interval, the resonant frequencies of the samples and of the quartz crystals differed by not more than 0.3%.

The F centers were photoionized by illuminating the sample with F light ($\lambda=470$ nm) for a specified time interval, using a DKSSh-500 lamp with an SPM-2 monochromator or a 170-W incandescent tungsten lamp and light filters. The employed samples satisfied the condition $\alpha d<0.3$, where α is the optical absorption coefficient and d is the sample thickness. Thus, the decrease of the light intensity on passing through the sample was negligible.

The experiments were performed at amplitudes corresponding to the amplitude-dependent internal friction (this was verified by plotting the amplitude dependence) at constant v_t.

The main part of the study was an investigation, at various temperatures, of the kinetics of the variation of the dislocation charge as a function of the incident-light intensity, of the illumination duration, and of the F-center concentration.

RESULTS OF EXPERIMENTS

When edge dislocations are introduced into a sample, the oscillating mechanical stress gives rise to an alternating voltage U corresponding to the charge q on the dislocation. In the estimate of q by formula (2), we assumed $N_2/N_1=1$. The dark charge is negative and remains practically unchanged when the sample is kept at 300 K for a rather long time. The photoionization of the F centers by the F light leads to a change in the dislocation charge. Figure 2 shows this change at $T=295$ K. When the light has sufficient intensity, the change of the dislocation charge goes through three stages. Stage I is an increase of the negative charge and is observed only in the presence of illumination. Stage II is a rapid decrease of the charge, with possible reversal of its sign; it is observed both in the course of illumination and after the light is turned off. Stage III is the restoration of the initial charge. The kinetics of the variation of the charge depends substantially on the temperature, on the intensity of the light, on the illumination duration, and on other parameters.

The dependence of the kinetics of the variation of the

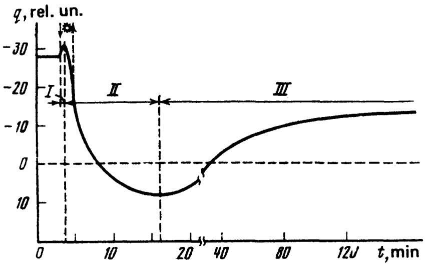

FIG. 2. Photostimulated change of the dislocation charge ($T=295$). The numbers I, II, III denote different stages of the change of the dislocation charge.

dislocation charge on the measurement temperature is shown in Fig. 3. The data pertain to the same sample at different temperatures. An important factor in measurements of this kind is the requirement that the initial conditions be identical for each temperature. To satisfy this requirement, the duration of the illumination with F-light was chosen in each measurement to be 10 sec. This time interval is short enough for the number of F centers not to decrease noticeably at the employed light intensity, and at the same time it is sufficient to cause a significant change of the charge. When measurements were made in the temperature interval below 300 K, the sample was heated to 300 K and kept at this temperature after each measurement cycle at a specified temperature, so as to restore the initial dark charge. The kinetics of the variation of the dislocation charge was practically identical for different samples but with the same initial data.

Figure 3 shows plots of the dislocation charge during the first hour after the light is turned off. We note that the course of stage I is practically independent of temperature. Stages II and III slow down substantially with decreasing temperature, and may not appear at all at sufficiently low temperatures. It is convenient to examine the character of the singularities of each of the stages separately.

Stage I. It is observed only with the light on. It manifests itself most clearly at low temperatures ($T<250$ K). As seen from Fig. 4, in this case the function $q(t)$, where t is the exposure time, is described by a curve with saturation. The quantity $q_{\max}$ corresponding to the saturation level for a given sample depends little on the temperature and on the concentration of the F centers. The independence of $q_{\max}$ of the intensity of the incident light is readily illustrated by an experiment (Fig. 4) in which light of higher intensity is subsequently turned on after the saturation level is reached. At the characteristic value for $q_{\max}$ for the samples employed in the experiments is 0.001–0.005 electron/site. It must be noted that even though $q_{\max}$ does not depend on the light intensity and on the F-center concentration, the rate at which the saturation level is reached increases substantially when these quantities are increased. The curve $q(t)$ during stage I is well approximated by an exponential with a time constant τ_1. This can be seen in Fig. 5, which shows the plots of $q(t)$ in the coordinates $\log\{(q_\infty - q)/(q_\infty - q_0)\}$ and t. The curves were plotted at 280 K, and at this temperature stage II is weakly pronounced. At change in the slopes of the straight lines, i.e., an increase of τ_1 is noted when the F-center concentration is decreased by discoloring the crystal. The values of τ_1 for different samples vary in the range 10–100 sec.

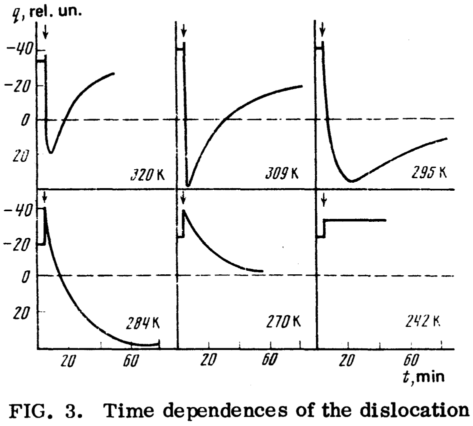

FIG. 3. Time dependences of the dislocation charge following a short-duration illumination at temperatures 240–320 K. Illumination time 10 sec. The turning on and off of the illumination is marked by a single arrow.

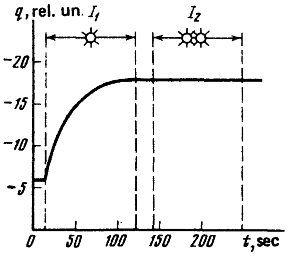

FIG. 4. Dependence of the dislocation charge on the time during stage I following illumination with light of varying intensities; I—intensity of incident light, $I_2=2I_1$, $T=232$ K.

We emphasize the following important circumstance. Regardless of the sign of the initial dislocation charge, stage I corresponds to an increase of the negative charge. This fact is illustrated by an experiment in which the light was turned on both when the dislocation charge was negative and when it became positive as a result of photostimulated sign reversal. In both cases the charge became more negative under illumination.

Stage II. This stage takes place both in light and after the light is turned off, and depends strongly on the tem-

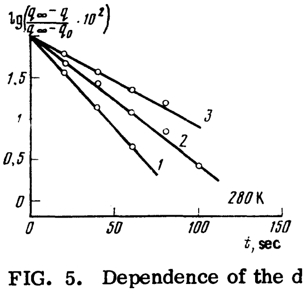

FIG. 5. Dependence of the dislocation charge on the time during stage I for one and the same sample with different F-center concentration. q_0 and q_∞ are the values of the dislocation charge at $t=0$ and at saturation. The concentration of the F centers in the initial samples is 1×10^{16} cm^{-3}. Curves 1, 2, and 3 were obtained as a result of discoloring the initial sample by light of the same intensity for 10, 80, and 220 sec respectively.

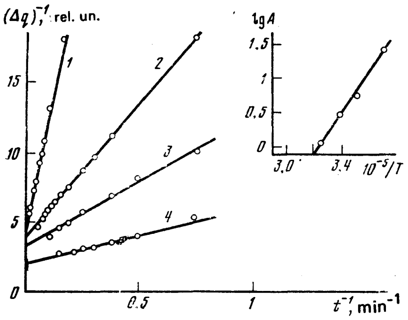

FIG. 6. Dependence of the dislocation charge during stage II on the time after the turning off of the light, in coordinates $(\Delta q)^{-1}$ and t^{-1}; curve 1—at 270 K, 2—at 284 K, 3—at 295 K 4—at 309 K. In the right corner is shown the plot of A (in relative units) against temperature $E = 0.55 + 0.5$ eV (Δq is the change of the dislocation charge after turning off the light).

perature, so that at low temperatures it may also not be observed (Fig. 3, $T = 242$ K). However, when a sample illuminated at $T < 250$ K is heated to room temperature, stage II occurs without additional illumination, and reversal of the sign of the charge can be observed.

The time dependence of the change of the charge Δq after turning off the light, with the exception of the values corresponding to the transition region between stages II and III, is described by the empirical relation (Fig. 6) $\Delta q = KAt/(K + At)$ or

$$(\Delta q)^{-1} = 1/K + 1/At. \tag{3}$$

In this expression, K and A are constants that characterize the depth and rate of the process. With increasing temperature, A increases in accordance with the Arrhenius law (see Fig. 6), with an activation energy 0.55 ± 0.5 eV, while K depends little on the temperature and increases with increasing exposure.

It should be noted that the acceleration of the stage II with increasing temperature can cause the stage I to become unobservable, owing to superposition of the processes responsible for stages I and II. A similar result is possible also in the case of a dark charge which is close to the limiting value.

As already indicated above, stage II can occur also in light. If the exposure times are long, the simultaneous occurence of stages I and II leads to stabilization of the charge as is well illustrated in Fig. 7. It is seen from the figure that the charge is stabilized, although the number of point defects per dislocation continues to increase, as follows from the change of the dislocation damping δ, which is sensitive to those defects that serve as pinning centers.

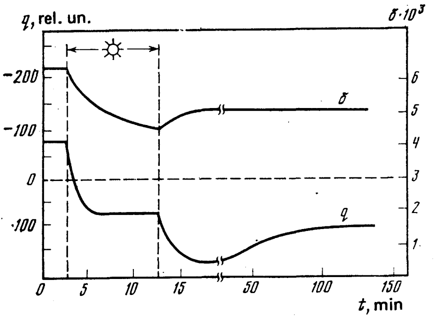

FIG. 7. Dependence of the dislocation charge q and of the ultrasound damping decrement δ on the time following prolonged illumination, $T = 295$ K.

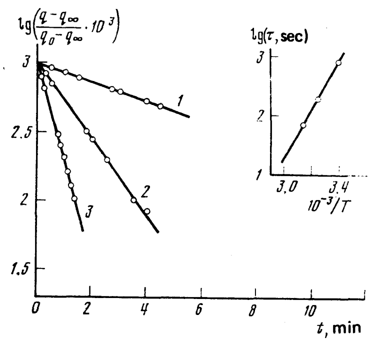

FIG. 8. Dislocation charge against time during stage III: 1—at 295K, 2—309 K, 3—320 K. In the right-hand corner is shown the dependence of the time constant τ_3 of stage III on the temperature; $E = 0.75 + 0.02$ eV.

Stage III. This stage is observed only after this lumination is stopped, and its course depends strongly on the temperature (Fig. 3). At negligible light sums, when the discoloring is small, this stage is well described by an exponential with a time constant that depends on the temperature in accordance with the Arrhenius law (Fig. 8), and with an activation energy ~ 0.75 eV. The attained level of restoration of the charge depends substantially on the prior action of the light on the sample. In the case of strong discoloring, the prime of restoration of the charge becomes substantially longer.

DISCUSSION OF EXPERIMENTAL RESULTS

It is known[3] that the geometry of the dislocations in AHC is such that charged steps (captured vacancies) can be produced on an edge dislocation. These steps can move together with the dislocation. For the sake of convenience we shall designate the vacancy density in the volume by n^- or n^+, and the densities on the dislocation line by ρ^- and ρ^+. Since both cation and anion vacancies can be frozen in the crystal, incomplete steps (captured vacancies) of opposite signs can be produced. The resultant dislocation charge is $q = (\rho^+ - \rho^-)e$. The limiting value of this charge is determined, on the one hand, by the elastic and electrostatic interaction of the dislocation with the vacancies, and on the other by the forces of the Coulomb interaction of the charges on the dislocation. According to Whitworth,[3] the limiting value in AHC is $q_{\max}$ 0.01 electron/site.

The dislocation charge under equilibrium conditions is screened by a Debye-Hückel cloud of oppositely charge point defects.[3] The screening radius λ, as well as the magnitude of the dislocation charge, depends strongly on the concentration of the vacancies of different types. At room temperatures, and lower, the concentration of the intrinsic point defects is low and the charge on the dislocation is determined by the vacancies introduced into the crystal to ensure its electroneutrality when doped by an impurity with different valence. In our crystal, according to chemical analysis, this impurity comprised divalent cation-replacing calcium ions, and therefore cation vacancies predominate in the crystal. Thus, one should expect the dislocations in such crystals to be negatively charged. This conclusion is confirmed by numerous experiments on crystals of similar kind.[3,9] It is also confirmed in our experiments. The charge in crystals without color centers is negative, and in the same crystals but with color centers the dark charge is likewise negative, although its value is somewhat lower.

We examine now the distribution of the charged point defects on the dislocations inside and outside the cloud that screens the dislocation charge, i.e., in the bulk of the crystal. As already indicated, in the volume of the crystal the concentration of the anion vacancies n^+ is very low, and the concentration of the mobile cation vacancies is n^-pN^+ (where N^+ is the concentration of the divalent cation-replacing impurity and p is the fraction of vacancies that are not bound into neutral $[N^+n^-]$ complexes), and is substantially larger than n^+. Because of the elastic (Cottrell) attraction, the concentration of both the anion (ρ^+) and cation (ρ^-) vacancies on the dislocation is larger than in the volume, but since there are still cation vacancies, we have $\rho^+ - \rho^- < 0$ and $q < 0$. The cloud that screens this dislocation charge is formed as a result of the increased impurity density compared with that of the free ions. Since the impurity ions are mobile only at temperatures much higher than room temperature, the necessary screening is reached as a result of the departure of unbound cation vacancies from the cloud, therefore their concentration in the cloud is lower than in the volume. The maximum charge attained in our experiments is $q_{\max} \sim 0.05$ electron/site, corresponding to a free cation vacancy concentration $\sim 10^{-8}$. At this vacancy concentration we have $\lambda \sim 10^{-5}$ cm. Since the density of the dislocations introduced is $N_1 \sim 10^6$ cm^{-2}, the radius of the Debye cloud turns out to be much less than the average distance between dislocation, the latter being 10^{-3} cm. This means that the Debye clouds of the dislocations do not overlap and that the proposed treatment of the distribution of the charged point defects is perfectly reasonable.

It should be noted that the irradiated crystals contained a large number of uncharged point defects, such as color centers, hole centers, etc., which in first approximation can be regarded as uniformly distributed over the entire volume, including the region inside the screening cloud.

The sequence of the photostimulated change of the charge on the dislocation can be visualized in the following manner. Illumination with F light results in photoionization of the F centers and formation of F^+ centers (anion vacancies) and photoelectrons. The lifetime of the electron in the band is short,[10] owing to the presence of capture centers in the crystal. It is known[11] that the principal capture centers in gamma-irradiated AHC are the chlorine atoms in interstices (the most effective traps, which lead in fact to a discoloration of the crystal), and F and F^+ centers. The presence of dislocations can lead to capture of photoelectrons by the dislocation traps. Such traps can be F and F^+ centers on the dislocation.[12] The capture of the photoelectrons on a dislocation is possible because of the presence, in the immediate vicinity of the dislocation, of an unscreened positive potential. In fact, the maximum attainable charge in our experiments was $q \sim 0.005$ electron/site. Since the concentration of the cation vacancies on the dislocation line greatly exceeds the concentration of the anion vacancies, the average distance between vacancies on the dislocation is a $\sim e/q = 0.8 \times 10^{-5}$ cm, which is not much less in order of magnitude than the radius of the screening cloud. Therefore at distances $< a$ the screening is not very effective. Thus, the positive potential near the anion vacancy on the dislocation is preserved at distances $< a$, and the electrons produced in this region can be captured by the dislocation, even if the latter carries a negative charge.

Photoionization of the F centers in the crystal, including those inside the screening cloud, gives rise to a large number of anion vacancies. Because of the elastic and electrostatic attraction of the negatively charged dislocation, the anion vacancies begin to flow towards the dislocation, causing the charge to be redistributed in it. As already indicated, the overwhelming part of the photoelectrons is captured by atoms in the interstices, therefore the number of vacancies generated by the light is much larger than the number of electrons that settle on the dislocation traps. The influx, on the dislocation, of the anion vacancies produced by the illumination leads not only to a compensation of the charge in excess of the negative dark charge, but also to a considerable decrease of the charge below the dark level. Understandably, this change of the charge on the dislocation should cause a corresponding response in the system of cation vacancies. However, since the concentration of the cation vacancies inside the screening cloud is much less than the volume concentration, the cation vacancies should be redistributed by diffusion from the volume. Thus, within the framework of the proposed scheme, stage I constitutes capture of the photoelectrons by the dislocation traps, stage II is the decrease of the dislocation charge on account of the arrival, at the dislocation, of anion vacancies produced by illumination, and stage III is the restoration of the equilibrium dark charge as a result of the redistribution of the cation vacancies in the system. All three stages are shifted in time and in space, so that, on the one hand, the mobility of the photoelectrons is much larger than the mobility of vacancies (stages I and II), and on the other hand the diffusion paths of the cation and anion vacancies differ significantly (stages II and III).

Since the mobility of the photoelectrons is much larger than the mobility of the vacancies, the change of the dislocation charge as a result of the illumination with F light can be described by the following expression:

$$\frac{dq}{dt} = \frac{q_{max} - q}{\tau_1} - \frac{q - q_0}{\tau_2} + \gamma_e \operatorname{div}(j^+ - j^-), \tag{4}$$

where $q_{\max}$ is the limited value of the charge reached in the experiment, j^- and j^+ are the densities of the fluxes of the cation and anion vacancies, γ is the coefficient of capture of the approaching vacancies by a dislocation, and e is the electron charge. In expression (4), the first term corresponds to capture of photoelectron by the dislocation traps, the second to the thermal release of the electrons from the dislocation traps, and the third describes the establishment of the equilibrium charge via redistribution of the vacancies in the system.

The flux densities are determined both by diffusion and by drift:

$$j^+=D^+\nabla n^+-n^+\mu^+\frac{\partial}{\partial r}(U^++e\varphi),$$
$$j^-=D^-\nabla n^--n^-\mu^-\frac{\partial}{\partial r}(U^--e\varphi), \tag{5}$$

where D^+ and D^- are the diffusion coefficients, U^+ and U^- are the energies of the elastic interaction of the dislocations with the vacancy, n^+ and n^- are the densities and μ^+ and μ^- are the mobilities of the anion (+) and cation (−) vacancies. The potential φ is determined from the Poisson equation

$$\nabla^2\varphi=-\frac{4\pi e}{\varepsilon}(n^+-n^-+N^+).$$

We analyze now expression (4). At low temperatures, $T<T_{cr}$, the mobilities μ^+ and μ^- are so small that the motion of the vacancies can be neglected. At $U^+\sim 0.8$ or $U^-\sim 0.8$ eV (Ref. 13) this condition is satisfied at $T<250$ K. Thus, the third term in (4) can be neglected. The second of the two remaining terms also does not play a substantial role, inasmuch as, judging from the experimental data (see Fig. 3, $T=242$ K), at these temperatures the dislocation charge remains unchanged for a rather long time when the light is turned off, i.e., no thermal destruction of the dislocation capture centers takes place at these temperatures. Thus, at $T<T_{cr}$ we have

$$\frac{dq}{dt}=\frac{q_{max}-q}{\tau_1},\qquad q=q_{max}-(q_{max}-q_0)\exp\frac{-t}{\tau_1}. \tag{6}$$

The value of τ_1 can be estimated from the following simple considerations. The rate of filling of the traps by photoelectrons is proportional to the number of the latter generated by the light per unit time, i.e., to the quantity $\Phi\alpha\beta$, where Φ is the light flux, α is the light absorption coefficient, and β is the quantum yield, and is inversely proportional to the total concentration n_0 of the traps in the crystal. If it is assumed that the effectiveness of all the traps in the volume is the same, then

$$\tau_1=n_0S/\Phi\alpha\beta. \tag{7}$$

Assuming $n_0=1\times10^{16}$ cm^{-3}, $\alpha=1$ cm^{-1}, $\beta=1$, $\Phi=2\times10^{13}$ photons/sec, and an illuminated area $S=0.2$ cm^2, we obtain $\tau_1=100$ sec, in sufficiently good agreement, under the assumptions made, with the estimates obtained in the experiment ($\tau_1=10$–100 sec).

The proposed model explains the experiments on the influence of the light intensity and of the degree of discoloration on the course of stage I. An increase of the light intensity decreases τ_1, as follows from (7). At the same time, the dependence of q_{max} on I (Fig. 4) is evidence of filling of all the allowed traps. The discoloring of the sample decreases α. At the same time, while a change does take place in the concentration n_0 of the volume traps, it is smaller than α, since the concentration of the traps exceeds the concentration of the F centers. It follows therefore that τ_1 should increase upon discoloration, as is in fact observed in the experiment (Fig. 5). It is known[14] that $\beta\sim1$ in the temperature interval 270–320 K, and since this is the only quantity in (7) that depends substantially on the temperature, it follows that τ_1 does not depend on temperature in the interval 270–320 K. Therefore, when the temperature drops below 250 K, one should expect stage I to slow down because of the decrease of β. Let us estimate the possibility of describing the increase of the negative charge on the dislocation by means of the capture of the photoelectrons generated when the F centers are destroyed inside the screening cloud. The maximum charge is $q_{max}\sim0.005$ electron/site. If the dark charge is close to zero then to ensure a change of charge amounting to 0.005 electron/site in the course of stage I at a dislocation density $N_1=1\times10^6$ cm^{-2}, the number of required electrons is $\sim10^{11}$ cm^{-3}.

At a screening-cloud radius $\lambda\sim10^3b$, the volume occupied by all the clouds in the crystal is $\pi N_1\lambda^2=5\times10^{-3}$ cm^3, i.e., at an F-center concentration 1×10^6 cm^{-3} the clouds contain 5×10^{13} cm^{-3} F centers, and this number is quite sufficient to generate the required number of photoelectrons.

At moderate temperatures, an essential role is played by processes governed by the mobility of the vacancies, i.e., those described by the third term in (4). The thermal release of electrons from the capture centers, described by the second term of (4), also takes place,[15] but does not play a decisive role in the determination of the kinetics of the change of the dislocation charge. The reason is that the capture of the photoelectrons by the anion vacancies leads to formation of F centers (the main process), which are stable at the experimental temperatures. The formation of the less stable F^- centers, while it does take place, is less probable than the formation of the F centers. Therefore the process of the decrease of the negative charge on account of the release of the electrons with F^- centers is possible, but is much less effective than the process connected with the migration of the anion vacancies. In fact, after the light is turned off, the dislocation charge decreases to a level much lower than the initial one (Fig. 2). We therefore confine ourselves hereafter to a consideration of only the third term of (4).

We consider first the processes that take place immediately after the light is turned off, when the influx of the cation vacancies can be neglected. In the absence of light, $dq/dt=0$ and $j^+=j^-=0$. Turning on the illumination leads to generation of anion vacancies, and in first-order approximation it can be assumed that the generation takes place uniformly over the entire volume. The exposure time should be chosen so short that the displacement of the anion vacancies is negligible during the period of illumination. In this case, at the first instant after the light is turned off, the diffusion flux of the anion vacancies remains unchanged, and the entire change of the charge is due to the increase of the drift flux produced by the forces of elastic and electrostatic interaction of the dislocations with the anion vacancy. Since $e\varphi \sim U^- - U^+ < U^-$, the main contribution to this force is made by the elastic interaction. Then, the calculation of the flux of the anion vacancies can be reduced to the known problem of formation of Cottrell atmospheres near the dislocation.[16] The concentration of the anion vacancies near the dislocation corresponds to a change Δq of the dislocation charge, and is described by the expression

$$\Delta q = \eta e n^+ (3U^+ \mu^+ bt)^{2/3}, \tag{8}$$

where η is a certain numerical parameter.

Subsequently the influx of the anion vacancies to the dislocation slows down and stops ultimately because of the accumulation of the space charge, the depletion of the number of anion vacancies, and the change of the electrostatic potential which becomes less attracting and even repelling if the charge on the dislocation has reversed its sign. The total change of the charge during stage II is determined mainly by the number of the newly produced anion vacancies, and should therefore depend strongly on the absorbed light sum and weakly on the temperature in the investigated interval; this is in good agreement with the experimental results (see Fig. 3). The duration of this stage should decrease with increasing temperature in accordance with (6), also in good agreement with the experimental results (see Fig. 6). Estimates of the duration of stage II in accordance with formulas (6) agree with the experimentally determined ones, and the temperature dependence of the parameter A in the empirical formula (3) for the description of stage II agrees qualitatively with the conlusions of formula (6). It should be noted, however, that the empirically determined activation energy of the process of charge change during this stage is somewhat lower (0.55 ± 0.5 eV) than given by formula (6) (~ 0.8 eV), as is typical of anion vacancies in NaCl.[13] This is most readily due to the simplified description of the stage II, wherein all the processes reduce to a single one—formation of Cottrell atmospheres. Nonetheless, the proposed model explains well qualitatively the features of the course of stage II under the considered conditions.

A somewhat different picture should be observed in the case of long exposure times. In this case the anion vacancies and the electrons land on the dislocation simultaneously, and this leads to stabilization of the charge (see Fig. 7). All the arriving anion vacancies become filled by electrons. If the light is turned off, then generation, and consequently capture of photoelectrons ceases, and since the influx of anion vacancies is conserved, the positive charge is increased.

As already shown, in the region inside the screening cloud, in the equilibrium dark case, the concentration of the cation vacancies is decreased. This means that the dislocation feels the response of the system of cation vacancies to the change of the charge after some delay, and the delay time can be roughly estimated to be the time of displacement of the anion vacancies by a distance equal to the radius of the screening cloud, i.e., this time is determined by the mobility μ^-. Since $n^- > n^+$, the dark charge is negative. Inasmuch as the employed exposures are short, it follows that to upset this relation an equilibrium charge should be established, after the light is turned off and the stage II terminates, by migration of the cation vacancies through the dislocation, i.e., a flux j^- is produced. The concentration n^- in expression (5) for j^- does not change, since it is determined only by the concentration of the introduced divalent impurities. The appearance of the flux j^- is due only to the change $\delta\varphi$ of the electric potential of the dislocation, i.e.,

$$j^- = -n^- \mu^- e \frac{\partial}{\partial r} \delta\varphi.$$

At the same time, $\delta\varphi$ can be expressed in terms of the concentration of the cation vacancies, on the basis of the Poisson equation

$$\nabla^2(\delta\varphi) = -4\pi e \Delta n/\varepsilon,$$

where Δn is the change of the equilibrium concentration of the charges on the dislocation relative to the concentration established at the end of stage II, and ϵ is the dielectric constant. Since $e\Delta n = \Delta q$, expression (5), with account taken of the fact that stage II has already passed, can be written in the form

$$\frac{d\Delta q}{dt} = -n^- \mu^- \frac{4\pi\Delta q}{\varepsilon}. \tag{9}$$

Putting

$$\varepsilon/4\pi\mu^- n^- e = \tau_3,$$

we obtain

$$d\Delta q/dt = -\Delta q/\tau_3,$$

whence

$$q = q_{\mathrm{eq}} + (q_0 - q_{\mathrm{eq}}) \exp(-t/\tau_3), \tag{10}$$

where q_0 is the charge corresponding to the end of stage II, and q_{eq} corresponds to the end of stage III. The relaxation time τ_3 is determined by the mobility and by the concentration of the cation vacancies, inasmuch as under the experimental conditions we have $\mu^- \sim \exp(-U_m^-/kT)$. During the same time therefore U_m^- can be estimated from measurements of the temperature dependence of stage III. In fact, as shown above, (see Fig. 8), the experimental results are described by an exponential, and the activation energy U of the process responsible for stage III turns out to be ~ 0.75 eV, in agreement with the activation energy U_m^- of the migration of the cation vacancies, as obtained in a number of studies[13,17] by measuring the electric conductivity, the dielectric losses, and others.

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Electric fields in a weakly doped compensated semiconductor

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We obtain the distribution function $F(E)$ of the electric field produced by charged donors and acceptors on neutral impurity centers in a weakly doped compensated semiconductor at absolute zero temperature. For the case of a low degree of compensation of the main impurity ($K \ll 1$), when the charged impurities are situated in the crystal in the form of individual pairs comprising an ionized donor and an ionized acceptor, we obtain an analytic expression for $F(E)$. At higher degrees of compensation (up to $K = 0.95$) the function $F(E)$ is obtained with the aid of computer experiments. The method of Efros *et al*. [J. Phys. C: Solid St. Comm. **22**, 623 (1977)] is used to realize in the computer the ground state of the model of a weakly doped compensated semiconductor. It is found that up to the highest investigated K the most probable electric field at the neutral impurity, a field corresponding to the maximum $F(E)$, is much less than the value that would be obtained if the charged impurities were disposed relative to each other and relative to the neutral impurities in a completely uncorrelated manner, so that $F(E)$ would correspond to a Holtsmark distribution. This result points to a a strong correlation between the charges in the considered disordered system.

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I. INTRODUCTION

In weakly doped compensated semiconductors at low temperatures, when all the carriers are frozen out (we consider for the sake of argument an n-type semiconductor with a donor density N_D and an acceptor density $N_A < N_D$), the uncompensated electrons are situated on the donors, so that a unit volume contains $N_D - N_A$ neutral donors, N_A positively charged donors, and N_A negatively charged acceptors. The static electric fields produced by the ionized donors and acceptors cause a Stark shift and a splitting of the levels of those impurity centers that had remained neutral and contribute to the impurity optical absorption. Since the electric fields at the different impurity centers are different, this effect leads to a broadening of the spectral lines of the impurity optical absorption and of the photoconductivity; this line broadening mechanism is decisive in many cases (the analogous effect of Stark broadening of spectral lines in a gas plasma is well known).

The usual approach[1-8] in the calculation of the Stark broadening of the spectral lines in weakly doped compensated semiconductors reduces to the following. It is assumed that the charged donor and acceptor distributions are perfectly random (uncorrelated) relative to the radiation-absorbing neutral donors. In this case the field distribution that determines the shape of the spectral lines is well known: it is described by the Holtsmark formula,[9,15] in which the concentration of the charged particles must be taken to be equal to $2N_A$. This approach is valid when the crystal temperature is much higher than the characteristic scatter of the levels in the impurity band. At not too large a compensation this scatter is of the order of the Coulomb energy of the interaction of the charges over the average distance between the impurities, i.e., $\sim e^2N_D^{1/3}/\varkappa$, where $\varkappa$ is the