# Change of charge states of centers in zinc sulfide crystals with dislocations

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The influence of plastic deformation on the intensity and relaxation kinetics of ESR spectra of photosensitive paramagnetic iron and chromium impurities in single-crystal zinc-sulfide crystals is investigated. It is shown that the "residual" $Cr^+$- and $Fe^{3+}$-center densities produced in ZnS crystals that contain dislocations are the result of Cr- and Fe-center charge exchange in the electric fields that surround immobile charged dislocations. A lower bound is obtained for the charge of an immobile dislocation in a ZnS crystal. A reversible decrease of the intracenter-luminescence intensity is observed in the course of active deformation of ZnS crystals. The time during which the charge of a moving dislocation relaxes to that of an immobile one is determined.

## 1. INTRODUCTION

It is now undisputed that dislocations that move in plastically deformed II–VI crystals are charged. The presence of electric charges on moving dislocations, and their dependence on the rate of plastic deformation, temperature, and impurity content of the crystal were investigated by several groups using various methods.[1–5]

No attention has been paid, however, to the important question of the presence and charges of immobile dislocations in II–VI crystals. In the present study we found that the electric fields of immobile dislocations influence the charge states of photosensitive paramagnetic Cr and Fe centers in zinc-sulfide crystals. We determined the radii of the Read cylinders, and estimated the linear charge density of an immobile dislocation.

We also studied the influence of charge dislocations on the photoluminescence (PL) of zinc-sulfide crystals. A decrease of the photoluminescence intensity during the time of plastic deformation of the samples was observed and investigated. The experimental data were used to estimate the radii ($R_{\text{eff}}$) of the Read cylinders surrounding the moving charged dislocation, and to ascertain the nature of the temperature dependence of $R_{\text{eff}}$. The charge-relaxation time of a moving dislocation after it had been stopped was determined.

## 2. SAMPLES. EXPERIMENT

We investigate zinc-sulfide single crystals grown from the melt by the Bridgman method and doped with iron ($7\cdot10^{-3}\%$), chromium ($5\cdot10^{-3}\%$), and aluminum. Samples measuring $2\times2\times4$ mm were cut from the ingots with a diamond saw, and their surfaces were polished with diamond paste. The samples were cut in such a way that the slip plane that was active during the deformation was inclined 45° to the deforming stress. Uniaxial plastic deformation at a constant rate $(1\text{–}5)\cdot10^{-4}\ \text{s}^{-1}$ was produced in an "Instron-TM-M-L" test stand. The ESR spectra were recorded with a "Radiopan" SE/X-2543 microwave spectrometer. The apparatus used to study the spectral properties of the samples in the course of the plastic deformation is described in detail in Ref. 3.

## 3. INFLUENCE OF IMMOBILE DISLOCATIONS ON THE CHARGE STATES OF PHOTOSENSITIVE PARAMAGNETIC CENTERS IN CRYSTALS

To observe electric charges on immobile dislocations, we studied the influence of plastic deformation on the intensity and relaxation kinetics of the ESR spectra of the photosensitive paramagnetic iron and chromium impurity centers in single-crystal ZnS samples. The Fe and Cr impurity atoms usually enter into the ZnS lattice as equal-charge substitutes for the $Zn^{2+}$ ions, i.e., in a doubly ionized form, $Fe^{2+}$ and $Cr^{2+}$. No ESR signal is observed from $Fe^{2+}$ and $Cr^{2+}$ centers in ZnS crystals. It is known that the occupied electron level connected with the $Fe^{2+}$ acceptor center is located 1.1 eV above the top of the valence band, while the $Cr^{2+}$ center is an ionized donor whose level lies 0.6 eV below the bottom of the conduction band.[6]

Irradiation of ZnS crystals with ultraviolet (UV) light of frequency close to the intrinsic-absorption edge produces electron-hole pairs whose holes are captured by the $Fe^{2+}$ centers to form $Fe^{3+}$ centers and whose electrons are captured by the $Cr^{2+}$ centers to form $Cr^{3+}$ centers. The ESR spectra of paramagnetic $Fe^{3+}$ and $Cr^{3+}$ ions with $3d^5$ electron configuration have been thoroughly investigated.[6] When the UV irradiation of ZnS:Fe,Cr crystals is stopped, the iron and chromium centers undergo a reverse charge exchange via thermal ejection of the electrons from the $Cr^+$ centers to the conduction band and their subsequent capture by the hole $Fe^{3+}$ centers. The kinetics of the decrease of the $Cr^+$ and $Fe^{3+}$ centers is uniquely determined by the decreased intensity of the ESR spectra of these centers and is illustrated in Figs. 1 and 2. It can be seen that the reverse charge exchange of the $Cr^+$ and $Fe^{3+}$ centers is completed within 10–15 minutes after the UV irradiation is switched off.

Our investigations have shown that a certain density of $Cr^+$ and $Fe^{3+}$ centers remains in a ZnS:Fe,Cr sample with dislocations after the UV radiation is turned off (Figs. 1 and 2). The "residual" density of these centers increases with the dislocation density in the sample. By way of illustration, Fig. 2 shows, for the same sample but different strains, the dependence of the $Cr^+$-center density on the time after the UV is

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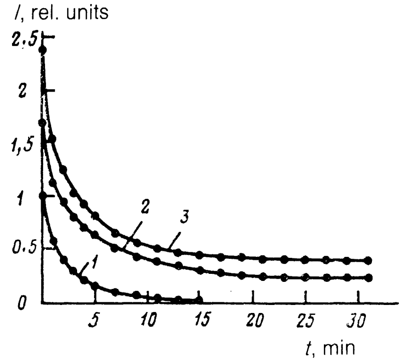

FIG. 1. Intensity of ESR spectral lines of $Cr^+$ centers vs the time after the UV irradiation is switched off, in plastically deformed ZnS crystals: 1—original sample, 2—sample strain 3.5%, 3—sample strain 6%.

turned off. It can be seen that increasing the plastic deformation increases not only the residual densities of the $Cr^+$ and $Fe^{3+}$ centers, but also the equilibrium densities of these centers in UV-irradiated samples.

To explain the preservation of the residual densities of the deep $Fe^{3+}$ acceptor centers and of the occupied $Cr^+$ donor centers, we examine the charge exchange between these centers in UV-irradiated ZnS crystals with dislocations. We have shown previously[3,4] that the valence and conduction bands are bent in the electric field surrounding charged dislocations. Regions of two types can therefore be arbitrarily distinguished in crystals with dislocations. In crystal regions of type I the electric fields of the dislocations are weak enough to be neglected. In regions of type II, which extend to the Read radius around the charged dislocations, the electric potentials of these dislocations must be taken into account.

In type-I regions, the charge exchange between the photosensitive paramagnetic iron and chromium centers is routine. In type-II regions the holes of the produced electron-hole pairs are captured by the $Fe^{2+}$ centers to form $Fe^{3+}$ centers, while the electrons are expelled from the type-II region to the type-I region in the radial electric fields that surround the immobile charged dislocation. Consequently, after the UV is switched off, the type-II regions adjacent to the dislocations will contain predominantly *p*-type $Cr^+$ centers, while the type-I regions between the dislocations will contain *n*-type $Cr^+$ centers. Knowing the residual density of the $Fe^{3+}$ centers we can estimate the radius $R_0$ of the Read cylinder surrounding the core of a charged dislocation.

The sample volume $\Delta V$ occupied by the Read cylinders adjacent to the dislocations is connected with the dislocation density $N_{\text{disl}}$ and with the sample volume $V_0$ by the relation

$$\Delta V=\pi R_0^2 N_{\text{disl}} V_0. \tag{1}$$

An expression for $\Delta V$ can in turn be easily obtained, given the number $N^0_{Fe^{3+}}$ of impurity iron centers that undergo charge exchange when the sample is illuminated, and the number $N^T_{Fe^{3+}}$ of the same $Fe^{3+}$ centers that remain in the crystal after the UV is turned off:

$$\Delta V=(N^T_{Fe^{3+}}/N^0_{Fe^{3+}})\, V_0. \tag{2}$$

From (1) and (2) we easily obtain an expression for the radius of the Read cylinder surrounding a charged immobile dislocation an a ZnS:Fe,Cr crystal:

$$R_0=[N^T_{Fe^{3+}}/(\pi N_{\text{disl}} N^0_{Fe^{3+}})]^{1/2}. \tag{3}$$

The number $N^0_{Fe^{3+}}$ of charge-exchanging impurity iron centers in ZnS:Fe,Cr with strain $\varepsilon\approx 3.5\%$, and the residual density $N^T_{Fe^{3+}}$ of these centers one hour after turning off the illumination, are respectively $N^0_{Fe^{3+}}\approx 6\cdot 10^{14}$ and $N^T_{Fe^{3+}}\approx 4.5\cdot 10^{13}$. The dislocation density in a ZnS crystal with strain $\varepsilon\approx 3.5\%$ is usually of the order of $N_{\text{disl}}\approx 3\cdot 10^8$ cm$^{-2}$. Substituting all these values in (3), we obtain the Read-cylinder radius $R_0\approx 10^{-5}$ cm. Note that it is just the Read cylinders which preserve, after the UV is turned off, the ionized iron centers that screen the electric field around charged immobile dislocations. Obviously, knowing the residual number $N^T_{Fe^{3+}}\approx 4.5\cdot 10^{13}$ of ionized iron centers we can estimate the linear charge density of an immobile dislocation. Indeed, in a $2\times 2\times 4$ mm sample at a dislocation density $N_{\text{disl}}\approx 3\cdot 10^8$ cm$^{-2}$, the total dislocation length is $L_{\text{disl}}\approx 6\cdot 10^6$ cm, and if the number of $Fe^{3+}$ centers remaining in the sample after the UV is switched off is $N^T_{Fe^{3+}}\approx 4.5\cdot 10^{13}$, the corresponding linear charge density of an immobile dislocation is $q\approx 0.25e$/site ($e$ is the electron charge).

Obviously, $q\approx 0.25e$/site is the lower-bound estimate of the immobile-dislocation charge, since this value was obtained assuming that only the $Fe^{3+}$ centers screen the electric potential of the dislocation. In the ZnS:Fe,Cr crystals investigated, the linear charge density of a moving dislocation, measured by the dislocation-current methods, is $q\approx 0.6$–$0.7e$/site and exceeds, as expected, the value $q\approx 0.25e$/site for an immobile dislocation. We believe the cause of this difference to be the fact that the charge of an immobile dislocation is screened both by ionization of the centers contained in the crystal and by diffusion of electrically active impurities and defects to the dislocations.

It should also be noted that, as proposed in Ref. 7, this difference can be due to the presence of a "dynamic" component of the charge on the moving dislocation.

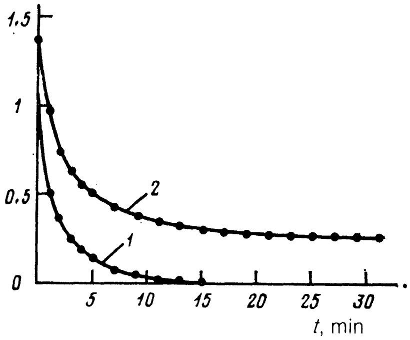

FIG. 2. Intensity of ESR spectral lines of $Fe^{3+}$ centers vs the time after the UV irradiation is switched off, in the original ZnS sample (curve 1) and in a sample with 3.5% strain (curve 2).

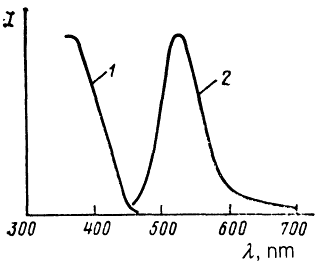

FIG. 3. Luminescence-excitation spectrum (curve 1) and PL spectrum (curve 2) of ZnS:Al crystal.

## 4. INFLUENCE OF ACTIVE DEFORMATION ON THE INTENSITY OF CRYSTAL PHOTOLUMINESCENCE

In the present study we investigated how active deformation affects the intensity of the intracenter luminescence of ZnS crystals. We observed a reversible decrease of the photoluminescence (PL) in the course of plastic deformation of ZnS single crystals. Temperature and spectral properties of PL quenching were investigated.

To determine the energy position of the levels connected with the luminescence centers, we investigate the PL spectra, the luminescence-excitation spectra, and the temperature dependence of the PL intensity in undeformed and in plastically deformed ZnS:Al samples. The PL and luminescence-excitation spectra of the investigated crystals are shown in Fig. 3. Analysis of the luminescence-excitation spectrum yielded an estimate of the depth of the luminescence-center ground state ($\Delta E_{\text{opt}} \approx 2.85$ eV). The temperature dependence of the photoluminescence intensity ($\lambda_{\text{PL}} \approx 525$ nm of a ZnS:Al crystal excited with $\lambda = 410$ nm light is shown in Fig. 4. It can be seen that the plot against temperature has two sections corresponding to activation energies $\Delta E_1 \approx 0.03$ eV and $\Delta E_2 \approx 2.8$ eV. The first of these energies is apparently due to thermal propulsion of the electron from the excited state of the center into the conduction band, i.e., it corresponds to the thermal depth of the excited state of the luminescence center. The activation energy $\Delta E_2 \approx 2.8$ eV agrees well with the optical depth of the luminescence-center ground state ($\Delta E_{\text{opt}} \approx 2.85$ eV).

We have reported this observation of a decrease of the PL intensity in the course of plastic deformation of ZnS:Al single crystals. Figure 5 shows the change of the PL intensity of such a sample during plastic deformation. It can be seen that at the instant when the plastic deformation begins the PL intensity decreases and remains practically constant during the entire deformation time. Once the active deformation is terminated and the sample is relaxed, the PL intensity rises again to its initial value $I_0$ within a time $\tau = 2 \cdot 10^2$ s. Consequently, a reversible decrease of the PL intensity takes place during the plastic deformation. No changes in the form of the PL spectrum are observed in the course of the plastic deformation.

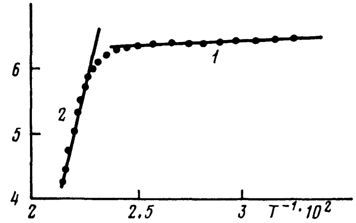

FIG. 4. Temperature dependence of PL intensity ($\lambda = 525$ nm) of ZnS:Al crystal excited with $\lambda = 410$ nm light. The activation energies on sections 1 and 2 are $\Delta E_1 = 0.03$ eV and $\Delta E_2 = 2.8$ eV, respectively.

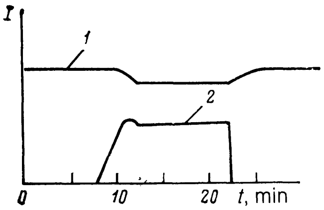

FIG. 5. Change of luminescence intensity of a sample that is being deformed: 1—luminescence intensity, 2—strain diagram.

The measurements show that the decrease of the PL intensity ($\Delta I / I_0$, where $I_0$ is the PL intensity in the unstrained crystal and $\Delta I$ is the change of the PL intensity during the plastic deformation) depends on the sample temperature. Raising the temperature decreases the effect of the plastic deformation on the PL intensity (Fig. 6). Thus, at a ZnS:Al deformation rate $\dot{\varepsilon} = 4 \cdot 10^{-3}\ \text{s}^{-1}$ the decrease of the PL intensity at 310 K is $\Delta I / I_0 \approx 0.14$, but is merely 0.045 at 380 K.

To explain the influence of plastic deformation on the PL intensity of ZnS crystals, we examine the course of the luminescence in II–VI crystals with dislocations. In type-I regions the PL follows the usual course. In type-II regions, an electron landing on an excited level of the center either undergoes radiative recombination and emits a photon, or tunnels into the conduction band in the electric field of the charged dislocation. Electron tunneling from the PL center into the conduction band produces a free electron, leaving an ionized center near the charged-dislocation core, i.e., the PL centers in type-II regions are ionized and there is no photoluminescence. Experimental and theoretical investigations of electron tunneling from centers into the conduction band in the electric field of a charged dislocation are described in detail in Refs. 4 and 7. In our earlier paper[4] we described the electron tunneling by using an approximation in which the dislocation potential was linear near the center. In that approximation, the probability of electron tunneling from an

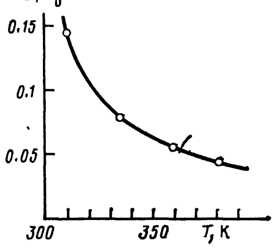

FIG. 6. Temperature dependence of the decrease of the PL intensity ($\Delta I / I_0$).

excited state of a center located at a depth $\Delta V_0$ below the bottom of the conduction band and at a distance $r$ from the dislocation core takes the form

$$W=\frac{qe\tau}{\varepsilon_0 r(2m^*\Delta V_0)^{1/2}kT}$$

$$\times\int_0^{\Delta V_0}\exp\left[-\frac{2}{3}\frac{(2m^*)^{1/2}\varepsilon_0 r(\Delta V_0-\varepsilon)^{3/2}}{eq\hbar}-\frac{\varepsilon}{kT}\right]d\varepsilon,$$

where $\tau$ is the electron lifetime in the excited state, $m^*$ the effective mass, $\varepsilon_0$ the dielectric constant, and $q$ the linear density of the dislocation charge. Calculations have shown that at $T=310$ K and at a dislocation charge density $q\approx 0.3$ $e$/site the effective radius is $R_{\text{eff}}\approx 10^{-2}$ cm. This means that for centers closer than $R_{\text{eff}}$ to the dislocation core the probability of electron tunneling from an excited state of the center into the conduction band is higher than the probability of its radiative recombination, i.e., all the PL centers located inside a cylinder of radius $R_{\text{eff}}$ around a charged dislocation are ionized and there is no photoluminescence. To obtain a correct theoretical estimate of $R_{\text{eff}}$ we must consider not only the tunneling, but also the inverse process, the capture of the free electrons by ionized field of the charged dislocation. Rigorous calculation of $R_{\text{eff}}$ with allowance for capture of electrons from the conduction band by ionized centers is a rather complicated task, but our experimental data on the temperature dependence of the PL quenching permit a quantitative estimate of $R_{\text{eff}}$ and cast light on its temperature dependence. In fact, knowing the PL intensity quenching $(\Delta I/I_0)$ we easily obtain the sample-volume fraction $(\Delta V)$ in which there is no luminescence:

$$\Delta V=(\Delta I/I_0)V_0, \tag{4}$$

where $V_0$ is the sample volume. At the same time

$$\Delta V=N\pi R_{\text{eff}}^2 V_0, \tag{5}$$

where $N$ is the density of the mobile dislocations. (At a plastic-deformation rate $\dot{\varepsilon}\approx 10^{-4}$ s$^{-1}$ and a sample temperature $T=300$–$400$ K the average mobile-dislocation density is $N\approx 3\cdot 10^6$–$10^7$ cm$^{-2}$.)

From (4) and (5) we easily obtain an expression for the radius

$$R_{\text{eff}}\approx(\Delta I/\pi N I_0)^{1/2}. \tag{6}$$

At a deformed-sample temperature 310 K and PL-intensity quenching amounts to $\Delta I/I_0\approx 0.14$, which corresponds, at a mobile-dislocation density $N=3\cdot 10^{-6}$ cm$^{-2}$, to the presence of an effective Read radius $R_{\text{eff}}\approx 1.2\cdot 10^{-4}$ cm. This value decreases if the temperature is raised. Thus, at a deformation temperature $T=380$ K the PL quenching effect is $(\Delta I/I_0)\approx 0.045$, corresponding to $R_{\text{eff}}\approx 0.7\cdot 10^{-4}$ cm.

As noted above, when the plastic deformation ends and the sample is unstressed the PL intensity increases to initial value within a time $\tau\approx 2\cdot 10^2$ s. This time is apparently the time in which the moving-dislocation charge relaxes to that of an immobile one. From our viewpoint, this relaxation can be related to screening of the dislocation-core charge by diffusion of ionized centers towards the core. At the same time, under the assumption advanced in Ref. 7 that the level of a moving dislocation is not uniformly occupied by electrons, this time $\tau\approx 2\cdot 10^2$ s can be the relaxation time of the nonequilibrium charge of the moving-dislocation core.

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