Dislocation exoelectron emission of colored alkali-halide crystals

A. V. Poletaev and S. Z. Shmurak

Institute of Solid State Physics, USSR Academy of Sciences

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We investigate the dependences of dislocation exoelectron emission on the temperature and on the *F*-center density in alkali-halide crystals. We show that the dislocation exoemission is an activation process, with respective activation energies 0.24, 0.44, 0.21, and 0.17 eV for KCl, NaCl, KBr, and LiF, respectively. Luminescence is observed when additively colored crystals are deformed. The results favor an Auger mechanism of dislocation exoemission. The dislocation velocities in the sample surface layers are estimated from an analysis of the experimental data.

Dislocations that are moved by plastic deformation influence strongly many physical properties of crystals.[1] Dislocation motion causes emission from II–VI semiconductors and from colored alkali-halide crystals (strain luminescence SL),[1–3] alters the crystal center structure,[2–4] enhances many luminescence bands (strain sensitization),[4] produces a dislocation current,[5,6] and so on. The foregoing and other processes, in which linear defects influence crystal properties, are due mainly to dislocations that move in the volume of the crystal, and can therefore be classified as volume processes. This approach disregards the motion of the dislocations in the crystal surface layer and of their interaction with the sample surface. This gap can be filled by dislocation exoelectron emission (DEE) which occurs when the dislocations move.[7] Indeed, the depth from which an electron can escape from the crystal in the course of exoelectron emission is 10^{-6} cm, so that it is expedient to use DEE to study the interaction between dislocations and centers located near and on the surface of the crystal, and to investigate the dynamic characteristic of dislocations in the surface layer of a sample.

Before employing DEE as a research method, however, it is necessary to investigate its mechanism in detail. This is indeed the purpose of the present study, devoted to the temperature characteristics of the DEE in colored alkali-halide crystals (AHC) and the dependence of the DEE on the *F*-center density; we estimate also the dislocation velocity as they emerge to the crystal surface. Our results favor the Auger mechanism proposed for the DEE by Molotskiĭ.[8]

EXPERIMENTAL TECHNIQUE

We investigated KCl, NaCl, KBr, and LiF crystals grown from the melt and not specially doped. The samples were chipped off the junction plane. A typical sample measured 3×5×15 mm. Color centers were produced by two procedures: photochemical coloring by γ or x-rays, and additive coloring. Photochemical coloring was carried out at 293 K using a Co^{60} source. The irradiation dose was varied in the range 10^4–10^7 rad.

Additive coloring was produced by heating the sample in the alkali-metal vapor at a temperature 100° below the melting point. The *F*-center density varied with the duration of the coloring. The number of centers in the samples was determined from the profile of the absorption band, using the Smakula formula.[9] Our samples showed after irradiation only one band corresponding to the *F* centers. The densities of the other electronic centers was negligibly small.

The emission was recorded with the setup described in Ref. 7. The sample was cooled by nitrogen vapor from a portable dewar in heat exchangers placed on the upper and lower punches. The temperature was regulated with heaters placed in the portable dewar and with a VRT-2 high-current temperature regulator. The temperature sensors for the VRT-2 were thermocouples placed on the upper and lower punches near the investigated sample. The temperature was maintained constant within $\pm 0.5°$ in the 300–90 K range.

The weak emission of the additively colored crystals was recorded with an FÉU-106 photomultiplier cooled to $-35°$ C and with a photon-counting system based on an NTA-1024 multichannel pulse analyzer. The number of noise pulses of the cooled photomultiplier was 1 count/sec at an anode sensitivity 1000 A/lum. The photomultiplier was cooled with an MTÉ-F thermoelectric microrefrigerator commercially produced in the USSR.

EXPERIMENTAL RESULTS AND THEIR DISCUSSION

According to the notions deduced from investigations of dislocation luminescence,[2] dislocations moved by plastic deformation capture electrons localized in electronic traps, such as *F* centers. If the center electron is localized in space, it becomes quasi-free when captured by a dislocation. The electron can move together with and along the dislocation.

The energy released when electrons captured by dislocations recombine with hole centers can ionize electrons localized on anion vacancies or captured by dislocations. This can cause electron emission. As shown earlier,[7] however, dislocation emission is observed both in photochemically and in additively colored crystals. The latter are known to have no hole centers and the described Auger process cannot account for the dislocation exoelectron emission of the samples investigated by us. Molotskiĭ[8] suggests that the centers at which the electrons liberated by the dislocations combine can be the deep traps present on the sample surface. Such traps are, for example, potassium ions adsorbed on an ideal surface of a KCl crystal. Such a trap is located 4.27 eV away from the bottom of the conduction band. The dislocation band in KCl is located at ~2.1 eV below the bottom of the

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conduction band. The described Auger process excites therefore a dislocation electron on the bottom of the conduction band. Further thermal ionization of these electrons gives rise to dislocation electron emission. It must be noted that the traps on which the dislocation-captured electrons recombine can also be volume and surface centers, for example interstitial Cl0 ions.

The DEE process can be schematically represented in the following form:

1) $D+F\to e_d$,
2) $(e_d+L)+e_d\to L^-+e$,
3) $e+T\to e^0$,

where L is the deep trap, e_d is an electron on the dislocation (D), and e and e^0 are electrons on the bottom of the conduction band and in vacuum, respectively.

TEMPERATURE CHARACTERISTICS OF DISLOCATION EXOEMISSION

If the Auger mechanism of DEE is realized, the temperature dependence of the dislocation exoemission is determined by two processes, viz., capture of F electrons by a dislocation (first stage) and thermal ionization of electrons located on the bottom of the conduction band (third stage). Investigations of dislocation luminescence have shown that capture of F electron by a dislocation is an activation process with an activation energy U_d coinciding with the activation energy of strain luminescence. The energy needed for thermal ionization of an electron from the bottom of the conduction band to the vacuum depends on the crystal electron affinity χ. The dislocation exoemission should therefore have an activation energy

$$U_{\rm DE}=U_d+\chi. \qquad (1)$$

The dependences of the DEE and of the dislocation luminescence of a KCl crystal are plotted in coordinates $\ln J$ and $1/T$ in Fig. 1. It can be seen from the figure that both DEE and SL are activated processes. The activation energy $U_{\rm DE}$ of the dislocation exoemission exceeds the activation energy U_d of the dislocation luminescence. For KCl crystals we have $U_{\rm DE}=0.25$ eV and $U_d=0.08$ eV. $U_{\rm DE}$ is the same for photochemically and additively colored crystals.

Similar temperature dependences of the DEE were obtained for the NaCl, KBr, and LiF crystals investigated by us in which, likewise, $U_{\rm DE}>U_d$. The values of $U_{\rm DE}$ for NaCl, KBr and LiF crystals are respectively 0.33, 0.21, and 0.17 eV.

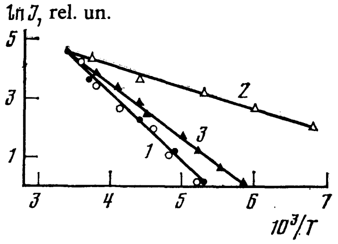

FIG. 1. Temperature dependences of the dislocation exoemission for KCl crystals: curve 1—dislocation exoemission (●—photochemically colored crystal, ○—additively colored crystal): curve 2—dislocation luminescence; curve 3—photostimulated exoemission.

To determine the values of χ in experiment we investigated the temperature dependence of the electron photoemission (EFE) stimulated by F light. The EFE intensity also decreases exponentially with decreasing temperature. For KCl the value of χ was found to be 0.16 ± 0.2 eV. It must be noted that our value of χ can differ from the true electron affinity, since the deformed samples have an alternating-sign mosaic of charges, and the field of the mosaic leads to local variation of χ.

Comparing the activation energies of the DEE, SL, and EFE processes we conclude that relation (1) is satisfied for KCl. This favors the Auger mechanism of dislocation exoemission.

DEPENDENCE OF THE DISLOCATION EXOEMISSION INTENSITY ON THE *F*-CENTER DENSITY

The number of electrons trapped by dislocations (n_d) is

$$n_d=vr\tau n_f, \qquad (2)$$

where v is the dislocation velocity, r the effective radius of interaction of the dislocations with the F center, τ the electron lifetime on the dislocation, and n_f and F-center density. The effective radius of the dislocation interaction with the F center and the electron lifetimes on dislocations were determined in Refs. 1 and 2. For a KCl crystal at $T=300$ °C their values are respectively $r\approx b$ (where b is the Burgers vector) and $\tau\approx3\cdot10^{-4}$ sec.

The number of electrons emitted by a plastically deformed crystal is

$$J=N\eta, \quad N=\dot{\varepsilon}n_d/b. \qquad (3)$$

According to Ref. 8

$$\eta=P_sP_0P_t, \qquad (4)$$

where $\dot{\varepsilon}$ is the rate of plastic deformation, P_s the probability of recombination of dislocation-captured electrons with deep traps, P_0 the probability of Auger ionization, and P_t the probability of thermal ionization of electrons from the bottom of the conduction band into the vacuum.

P_s is defined as

$$P_s=\sigma_sn_s, \qquad (5)$$

where σ_s is the recombination cross section and n_s is the density of the deep surface traps. The probability P_0 of observing at least one dislocation in a segment $2R_0$ equal to double the Auger-ionization radius (R_0) is[8]

$$P_0=1-\exp(-2R_0/R_d), \qquad (6)$$

where $R_d=(rn_jv\tau)^{-1}$ is the average distance between the electrons on the dislocations.

The probability P_t of thermal ionization of an electron is defined as

$$P_t=\omega_0\tau_0\exp(-\chi/kT), \qquad (7)$$

where ω_0 is a frequency factor and τ_0 is the lifetime of an electron in the conduction band. The density of electron flow out of the crystal in the course of plastic deformation is found from (2)–(7) to be

$$J=\alpha n_f[1-\exp(-\beta n_f)], \qquad (8)$$

where

$$\alpha=\frac{\dot\varepsilon}{b}n_s\sigma_s\tau v r\omega_0\tau_0\exp\left(-\frac{\chi}{kT}\right), \quad \beta=2R_0\tau v r. \qquad (9)$$

In the derivation of (8) no account was taken of the Auger ionization of the F centers, since its probability is considerably lower than P_0 (Ref. 8). It follows from (8) that at $n_f \ll (2R_0\tau v r)^{-1} = \beta^{-1}$ the DEE is proportional to n_f^2, and if the inequality is reversed ($n_f \gg \beta^{-1}$) the intensity is a linear function of the F-center density.

The experimentally obtained relation between the dislocation exoemission intensity and the F-center density is shown in Fig. 2. The figure shows it to be nonlinear. It can therefore be approximated by the function (8), by choosing the values of α and β such that the theoretical relation comes as close as possible to the experimental. It follows from Fig. 2 that at $\alpha = 1.5 \cdot 10^{-15}$ cm^{-3} and $\beta = 1.7 \cdot 10^{-17}$ cm^{-3} the agreement between the experimental curve and the theoretical Eq. (8) is quite satisfactory. This indicates that the DEE is a consequence of the discussed Auger process.

An important consequence of the considered Auger mechanism of the DEE is the presence of an emission band in additively colored crystals, with a maximum located in the region of the transition of the dislocation electron to a deep electron trap. In KCl this energy is ~2 eV (λmax = 6000 Å).[8] The radiation produced by plastic deformation of additively colored KCl crystals was observed by us in experiment. Owing to the weak emission intensity ($J \approx 10^4$ photons/cm^2 · sec at an F-center density $n_f = 5 \cdot 10^{17}$ cm^{-3} and at a deformation rate $\dot\varepsilon = 10^{-4}$ sec^{-1}) we were unable to determine exactly the position of the maximum of the emission band. An analysis of the spectral composition of the emission by using band filters allowed us to place the maximum of the emission in the 5800–6400 Å region.

The agreement of the experimental temperature and density dependences with the calculated ones and the presence of luminescence of additively colored samples is evidence that dislocation exoemission of electrons is indeed a consequence of an Auger process. For a final determination of the type of center participating in the DEE process it is necessary to establish the spectral composition of the radiation emitted when the dislocation-liberated electrons combine with deep traps on the surfaces of additively colored crystals.

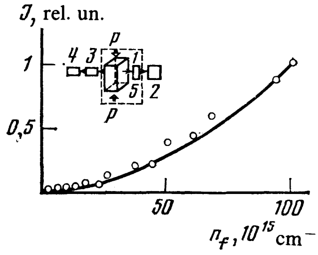

FIG. 2. Dislocation-exoemission density vs F-center density: points—experimental data, solid line—plot of $J = \alpha n_f[1 - \exp(-\beta n_f)]$ at $\alpha = 1.5 \cdot 10^{-15}$ cm^{-3} and $\beta = 1.7 \cdot 10^{-17}$ cm^{-3}. The inset shows the setup for loading the crystal and recording the dislocation exoemission with a VÉU-6 secondary electron multiplier (1) and the dislocation luminescence with the FÉU-106 photomultiplier (2) of the NTA-1024 multichannel analyzer (2, 4); 5—vacuum chamber.

QUANTITATIVE ESTIMATES

After determining in experiment the activation energy of the DEE process, calculating the constants α and β [(8), (9)] from the dependence of the dislocation exoemission intensity on the F-center density, and calculating the number of photons emitted following deformation of additively colored crystals, it becomes possible to estimate quantitatively a number of important parameters. Some are, for example, the velocity v of emergence of a dislocation to the surface, the density n_s of deep electronic traps, and the quantum yield of the strain luminescence of additively colored crystals.

The experimental value of the coefficient $\beta = 2R_0 v\tau r$ is $1.7 \cdot 10^{-17}$ cm^{-3}. Putting $R_0 = 5 \cdot 10^{-7}$ cm (Ref. 8), $r = 3 \cdot 10^{-8}$ cm, and $\tau = 3 \cdot 10^{-4}$ sec we get $v = 1.9$ cm/sec. The quantity v obtained in this manner is the dislocation velocity in a surface layer $\sim 10^{-6}$ cm (the depth from which an electron can be emitted).

Let us estimate the dislocation velocity v_0 in the interior of a sample. It is known that

$$\dot\varepsilon = Lv_0 b/2\Omega,$$

where Ω is the volume of the sample, $L = N_d a$ the total length of the moving dislocations, U_d is the number of moving dislocations, and a the linear dimension of the sample.

The number of moving dislocations, as well as their density, depends on the degree of deformation of the crystal. Assuming $N_d \approx 10^6$ cm^{-2} (Ref. 10) for $\varepsilon \approx 1\%$ and $\dot\varepsilon = 10^{-4}$ sec^{-1} (these are the values of ε and $\dot\varepsilon$ for which $J = J(n_f)$ plot of Fig. 2 was obtained), we get $v_0 \approx 10^{-2}$ cm/sec. Thus, the dislocation velocity in the surface layer v is larger by two orders of magnitude than the average dislocation velocity v_0 in the volume of the crystal. This is not surprising, since the velocity of the dislocation emerging to the surface is determined mainly by image forces and can exceed considerably the dislocation velocity in the interior of the sample.[11]

The radiation intensity in plastic deformation of additively colored samples is determined from the relation[8]

$$J_L = \eta\frac{\dot\varepsilon}{b}rv\tau\sigma_s n_s n_f, \qquad (10)$$

where η is the luminescence quantum yield. Using this equation we can determine from the experimentally measured intensity J_L and from the calculated coefficient α:

$$\eta = \frac{J_L}{\alpha n_f}\omega_0\tau_0\exp(-\chi/kT); \qquad (11)$$

assuming $\omega_0 = 6 \cdot 10^{13}$ sec^{-1} and $\tau_0 = 10^{-7}$ sec we obtain $\eta = 1.33 \cdot 10^{-3}$. This value is smaller by an order of magnitude than the intracenter luminescence (IL) of Cu$^+$ centers in KCl:Cu (Ref. 4) and agrees with the IL quantum yield of the centers participating in this process.

Dislocation exoemission of electrons can serve also as a method of determining the density n_s of the surface traps. Indeed, it is easy to determine n_s from (10): by putting $\sigma_s = 5 \cdot 10^{-13}$ cm^2 (Ref. 8) we get $n_s \approx 1.6 \cdot 10^9$ cm^{-2}. The obtained value of n_s is much less than the limiting density of the surface traps. Therefore the deep electron traps in the subsurface region and on the surface can indeed serve as recombination centers for the dislocation electrons, and the energy released in this process can go to excitation of other dislocation electrons into the conduction band, followed by thermal activation into the vacuum.

Thus, the Auger mechanism of electron exoemission from semiconductors and dielectrics, first considered by Tolpygo and Sheinkman,[12] describes also the dislocation electron exoemission produced when colored alkali-halide crystals are deformed.

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