

Decay of excitons into defects and polarized luminescence produced as a result of recombination of the defects in CsBr

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The decay of photon produced excitons into Fresnel defects (F and H centers) was observed in CsBr crystals at 4.2 K. The reverse process—light-or heat-stimulated recombination of H centers with F centers—leads to the production of autolocalized excitons that give a characteristic, 3.5-eV, polarized luminescence.

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The decay of autolocalized excitons (ALE) with the production of neutral Fresnel defects (F and H centers) has recently been observed for face-centered cubic KBr crystals.^{1,2} It was proved by the EPR method that the ALE is an electron (e) in the field of an autolocalized hole (a Br_2^- molecule occupying two anion sites), an H center is this

Br_2^- molecule occupying one anion site of the lattice, and an F center is an electron in the field of an anion vacancy (see, for example, Refs. 1 and 2).

We have observed at 4.2 K the decay of ALE with the creation of F and H centers in body-centered cubic CsBr crystals. We have also observed for the first time the polarized photostimulated and thermally stimulated luminescence of ALE that accompanies the destruction of H centers, which is interpreted as the result of radiative recombination of Fresnel defects.

The CsBr crystals with an impurity content of less than 10^{15} – 10^{16} cm^{-3} were grown after a 40-fold zone refining. The crystal, cut along the $[100]$ planes, was excited along the $[001]$ direction in a VUF immersion helium cryostat by the radiation of a hydrogen discharge through a VMR-2 monochromator (intensity of 10^8 – 10^9 photons $\cdot \text{cm}^{-2} \cdot \text{sec}^{-1}$ and a time of 10^1 – 10^4 sec). The luminescence was recorded along the $[010]$ direction via an MDR-2 monochromator by a cooled FEU-106 that operated in the photon-counting mode. Photostimulation was accomplished in the $[001]$ direction via a DMR-4 monochromator. Polaroid films were used as a polarizer and an analyzer.

Curve 1 in Fig. 1 shows the excitation spectrum measured at 4.2 K (equal number of photons) for the 3.5-eV luminescence, which, according to Ref. 3, corresponds to the radiative annihilation of triplet ALE (the $^3\Sigma_u \rightarrow ^1\Sigma_g$ electron transitions in a Br_2^- molecule). The ALE luminescence is efficiently excited in the intrinsic-absorption region, where the free excitons with $n = 1, 2$ (6.8–7.2 eV) and the separated electrons and holes ($h\nu > E_g = 7.25$ eV) are produced.

It has been shown⁴ that stable F centers (1.95 and 2.15-eV absorption bands) and H centers (2.53 and 2.84-eV bands) appear after the irradiation of CsBr by particles or high-energy quanta at 10 K. We have observed the appearance of F and H centers after the irradiation of CsBr by 6–8 to 7.2-eV photons that selectively produce the excitons. As follows from Fig. 1 (curve 2), the 3.5-eV luminescence is excited in the irradiated crystals not only in the $h\nu > 6.8$ -eV region but also by 1.5 to 3.0-eV photons.

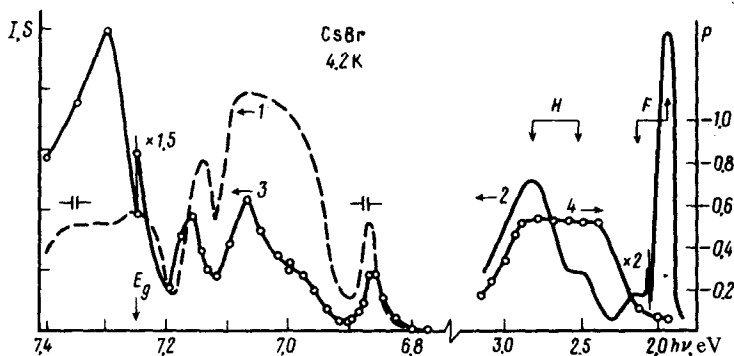


FIG. 1.

The photostimulated luminescence (PSL) of autolocalized excitons appears as a result of absorption of light by the F centers (1.95 and 2.15 eV) and by the H centers (2.50 and 2.82 eV).

Curve 1, in Fig. 2 shows the data for thermally stimulated luminescence (TSL) in the 3.5-eV region that accompanies the annealing of H and F centers. The crystal was heated at a rate of 1 K/min after the irradiation by 7-eV photons. As a special investigation showed and, in particular, an investigation of the annealing of H centers (see curve 2 in Fig. 2), the 11, 13, and 18 K TSL peaks correspond to the jump diffusion of H centers and to their recombination with the F centers that are localized at different distances from the H centers. The most intense peak at 11 K corresponds to recombination of the adjacent H and F centers, which are efficiently produced due to the exciton decay.

Curve 3 in Fig. 1 shows the spectrum for formation of H centers by an equal number of photons of different frequencies (10^{10} photons·cm⁻²). The relative number of H centers was determined from the 3.5-eV PSL flux for illumination by 2.8-eV photons, which stimulate the jump diffusion of H centers. The formation spectrum of H centers in the 6.8 to 7.2-eV region indicates that at 4.2 K the excitons with $n = 1$ and 2 in CsBr decay with the production of H centers. The H and F centers are also produced as a result of recombination of electrons with autolocalized holes ($h\nu > 7.25$ eV).

The decay of ALE ($\text{Br}_2^- e$) into defects is schematically illustrated in the inset of Fig. 2. The Br_2^- molecule, which initially (t_1) occupies two anion sites, is displaced (t_2, t_3) to one site (an H center is formed), and the electron remains localized near the second site (an F center is formed).

The similarity between the PSL and TSL emission spectra for the irradiated CsBr and the emission spectrum of the triplet ALE (3.5 eV) in the direct production of

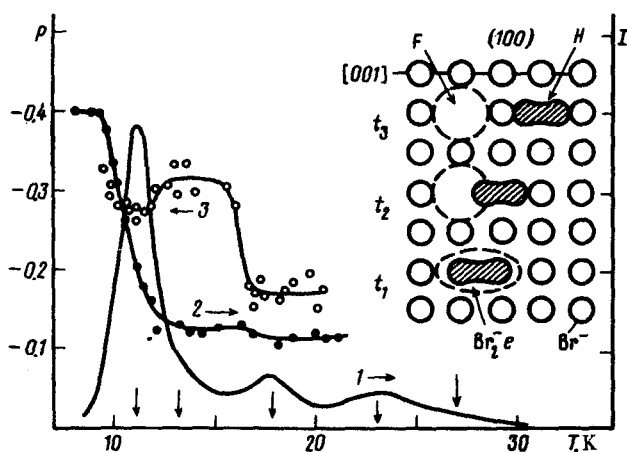


FIG. 2.

excitons by 6.8 to 7.2-eV photons is of special interest. This led to the hypothesis that photostimulated and thermally stimulated recombinations of H centers with F centers lead to the formation of ALE, i.e., inverse process of the ALE decay into defects. As the inset in Fig. 2, shows, the orientation of Br_2^- is preserved in the CsBr crystal in the recombination of the adjacent H and F centers (processes $t_3 \rightarrow t_2 \rightarrow t_1$), and a polarized luminescence of the ALE is expected to occur as a result of photostimulated or thermally stimulated annealing of the defects.

According to this model, a 3.5-eV *polarized* luminescence, which is characteristic of fourth-order emitters oriented along the axes, is produced as a result of pumping of an irradiated crystal (2.8 eV) that has been linearly polarized along [100]. Curve 4 in Fig. 1 represents the spectral dependence of the degree of PSL polarization $P = (I_{100} - I_{001}) / (I_{100} + I_{001})$. $P = -0.5$ in the region of the absorption bands of the H centers. The appearance of luminescence with $P < 0$ is attributable to the fact that absorption of the stimulating light is allowed in the axial direction of the Br_2^- molecule,⁴ and the radiative transition (3.5 eV) for the ALE is allowed in the plane that is perpendicular to the axis of a molecule.³

If the orientation of 2/3 of the H centers is disturbed by 2.8-eV photons (in addition to the centers oriented in the direction of propagation of the illuminating light [001]) after irradiation by 7-eV photons, then the 3.5-eV luminescence will turn out to be polarized when the TSL is measured in the [010] direction. The temperature dependence of P is represented by curve 3 in Fig. 2. The H centers, which remain after the pumping, are orientationally recombined with the F centers. $P = -0.3$ as a result of recombination of the adjacent H and F centers (the 11 K TSL peak). The degree of polarization is lower for the H and F centers with greater separation (the 18 K TSL peak), since a partial reorientation of the H centers occurs as a result of their multiple jumps.

Complex alternative explanation of the ALE luminescence due to a jump diffusion of H centers involves the interaction of these centers with the radiation or pre-radiation defects, rather than the F center. Our experiments with very small irradiation doses (10^9 photons·cm⁻²) showed, however, that the 11-K TSL peak with the characteristic 3.5-eV emission (ALE luminescence in the $^3\Sigma_u \rightarrow ^1\Sigma_g$ transitions) can be detected even when the F and H pairs are completely isolated from each other and from the other radiation defects.

Unsuccessful attempts to detect luminescence during the recombination of the H centers with the F centers were previously made for KCl and KBr.⁵ The energy of the relaxed ALE in CsBr is close to that of the F and H pair, which makes it possible for the ALE $\longleftrightarrow F + H$ reaction to proceed in both directions. The luminescence of ionic crystals due to recombination of electrons with the holes has been known for a long time and has been thoroughly investigated. We have observed certain characteristics in CsBr, which can be explained as luminescence due to recombination of Frenkel defects (H and F centers).

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