Optical detection of EPR of self-trapped excitons using photostimulated luminescence of crystals

N. G. Romanov, V. A. Vetrov, and P. G. Baranov

A. F. Ioffe Physicotechnical Institute, Academy of Sciences of the USSR

Optically detected EPR spectra are recorded for the first time using photostimulated luminescence of crystals. The mechanism of the formation of self-trapped excitons in fluorite crystals is clarified.

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Optical excitation in absorption bands of radiation centers in ionic crystals leads to photostimulation of luminescence (PSL), which could be due to various recombination processes. The effect of a magnetic field on PSL in alkali-halide crystals was studied in Ref. 1. In this work, optically detected EPR (OD EPR) spectra are recorded for the first time, using PSL in ionic crystals. The technique of OD EPR based on PSL is used to study triplet self-trapped excitons (STE) in fluorite crystals. Such investigations are of interest because the mechanism of formation of STE in crystals is not yet completely understood.

We used nominally pure CaF_2, SrF_2, and BaF_2 crystals, irradiated with x rays at a temperature of 77 K. Self-trapped holes (V_k centers), as well as electronic color centers with absorption bands in the visible region, occur in such crystals.[2] When these bands are excited, PSL in the UV region is observed (Fig. 1, curve 1). The PSL spectrum contains a band with maximum at 290 nm, which is attributed to STE emission.[2,3] Optically detected EPR spectra were recorded from the intensity of PSL at a temperature of 2 K in the 8 mm rf region with the rf field modulated in a resonator with frequency varying from 100 Hz to 2 kHz.

In a magnetic field at low temperature, the intensity of PSL decreases, but this decrease is an order of magnitude smaller than in the case of tunneling recombination afterglow.[4] In the presence of an rf field, optically detected EPR signals, which are associated with singlet recombination of electronic and hole centers and which correspond to the ground states of the recombining centers, can be measured from the PSL intensity. Such a recombination can be optically stimulated because of the formation of close pairs of recombination centers as a result of charge transfer.

Optically detected EPR spectra of triplet STE were recorded from the intensity of PSL in CaF_2, SrF_2, and BaF_2 crystals. For CaF_2 crystals, the EPR spectra, which are represented in Fig. 1 by curves 2 and 3 and which correspond to crystal orientations $B \parallel [111]$ and $B \parallel [110]$, were obtained from the PSL band with maximum at 290 nm. For SrF_2 and BaF_2 crystals, optically detected EPR spectra recorded from the PSL are analogous to the spectra for CaF_2.

Optically detected EPR spectra of self-trapped excitons were observed also in x-ray irradiated (at 77 K) CaF_2: Mn crystals with photostimulation in the band of Mn^+
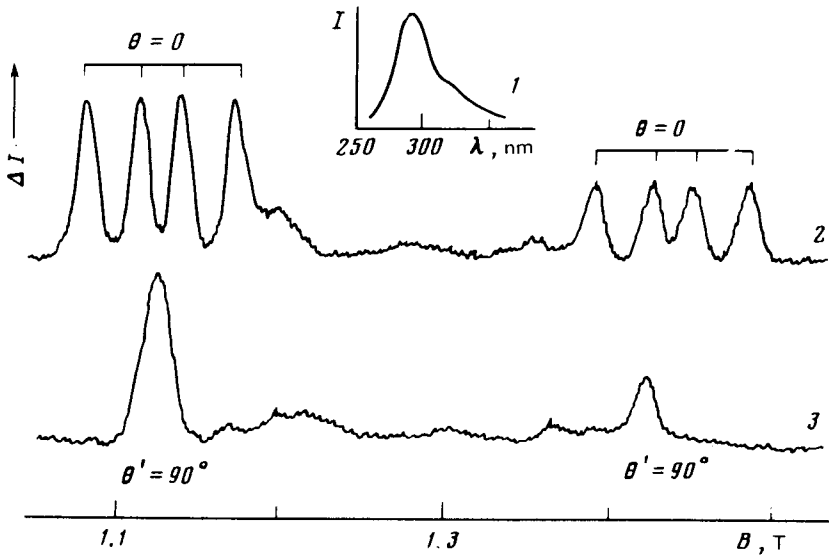
FIG. 1. PSL spectrum of a CaF$_2$ crystal with excitation at 510 nm; 2, 3 optically detected EPR spectrum recorded from the PSL intensity of x-ray irradiated (at 77 K) CaF$_2$ crystal, $T = 2$ K; $\nu = 35.1$ GHz; the frequency of modulation of the microwave field is 1 kHz; the crystal orientation is $B \parallel [111]$ (curve 2) and $B \parallel [110]$ (curve 3). θ is the angle between the axis of the self-trapped exciton and the orientation of the magnetic field.

centers. Investigations of optically detected EPR based on PSL showed that in addition to STE emission, PSL in the UV region arises due to photostimulated recombination of electronic and hole centers (in particular, Mn^+-V_k), comprising approximately 30% of the total intensity of the PSL, as well as due to emission from excited states of impurity defects.

The optically detected EPR spectra of self-trapped excitons obtained here are described by the spin Hamiltonian

$$\mathcal{H} = \beta\, \mathbf{H}\overset{\leftrightarrow}{g}\mathbf{S} + D\,(S_z^2 - \frac{1}{3}S(S+1)) + E(\,S_x^2 - S_y^2\,) + \mathbf{S}\overset{\leftrightarrow}{A_1}\mathbf{I}_1 + \mathbf{S}\overset{\leftrightarrow}{A_2}\,\mathbf{I}_2$$

where $S = 1$, and $\overset{\leftrightarrow}{A}_1$ and $\overset{\leftrightarrow}{A}_2$ are the tensors of the hyperfine interaction of unpaired electrons of self-trapped excitons with nonequivalent fluorine nuclei with spins $I_1 = I_2 = 1/2$. The orientation of the axes is $z\parallel[111], x\parallel[110], y\parallel[11\overset{..}{2}]$. The following spectral parameters were obtained for self-trapped excitons in CaF$_2$ crystals: $D = 0.154$ T; $E = 0.046$ T; $g_z = 1.98$; $g_x = g_y = 1.99$; $A_{1z} = 0.0576$ T; $A_{2z} = 0.0337$ T; $A_{1x} \approx A_{2x} < 0.003$ T. The quantities A_{1y} and A_{2y} are close to the corresponding quantities A_{1z} and Z_{2z}. From the orientational dependences of the optically detected EPR spectra it follows that the symmetry axis of self-trapped excitons is oriented along the crystal axis $\langle 111 \rangle$ and, in addition, the axial symmetry is strongly distorted. The hyperfine interaction with fluorine ions has a sharp anisotropy in the plane $\{111\}$.

Optically detected EPR spectra of self-trapped excitons are observed with photostimulation in the absorption bands of electronic centers in crystals in which the hole centers are self-trapped holes. This is indicated by the fact that self-trapped excitons
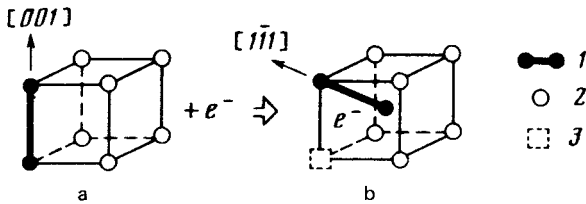
FIG. 2. Models of self-trapped holes. V_k centers (a) and self-trapped excitons (b) in fluorite crystals. 1 F_2^- molecular ions; 2 F^- ions; 3 anionic vacancy.

are formed as a result of capture of excited electrons by V_k centers. The participation of V_k centers in the process of formation of self-trapped excitons is likewise indicated by the absence of both the PSL band with maximum at 290 nm and the optically detected EPR spectra of self-trapped excitons in crystals heated to a temperature at which V_k centers are destroyed. Since a self-trapped hole (V_k center) has an axis of symmetry $\langle 100 \rangle$, while the self-trapped exciton has the symmetry axis $\langle 111 \rangle$ and the axial symmetry is strongly distorted, we conclude that as an electron is trapped and a self-trapped exciton is formed, relaxation occurs. As a result, the axis of the molecular ion rotates by an angle $\sim 35°$ in one of the planes $\{110\}$. In this case, one of the two fluorine ions is displaced into an unoccupied interstice. As a result, the spin density in the molecular ion F_2^- is redistributed because the fluorine nuclei are no longer equivalent. Models of the initial and final stage of the relaxation process are shown in Fig. 2. With the displacement of a F^- ion into an interstice, an anionic vacancy forms in the nearest neighborhood of F_2^-, causing a distortion of the axial symmetry of the self-trapped exciton. The only possible mutual position of the molecular ion F_2^- and the anionic vacancy is shown in Fig. 2b.

It should be noted that with recombination of the self-trapped exciton, whose model is shown in Fig. 2b, there is a finite probability for a stable pair of *F-H* centers to form, similar to the manner in which this occurs in alkali-halide crystals.[5]

The results obtained in this work explain the process of formation of self-trapped excitons and the nature of the UV band of x-ray luminescence of crystals such as fluorite. The action of ionizing radiation leads to the formation of V_k centers, which, by capturing electrons, are transformed into self-trapped excitons with the optically detected EPR spectra shown in Fig. 1. In this case, it is no longer necessary to assume the formation of close *F* and *H* centers during radiolysis to explain the structure of the self-trapped exciton.[3,6]

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