

SELF-TRAPPED EXCITONS IN LOW-SYMMETRY FLUORIDE CRYSTALS

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Triplet self-trapped excitons have been detected in low-symmetry crystals of the fluorides BaFCl₄, BaFBr, and LaF₃. In BaFBr crystals two types of excitons, on-center and off-center (with a symmetric or displaced configuration). The slow initiation of exciton luminescence in BaFBr is associated with the barrier transition from an on-center to an off-center configuration. In LaF₃ crystals tunnelling population of the exciton state also appears in the initiation. In LaF₃ crystals excitons appear only in the luminescence and excitation spectra while in the absorption spectra the exciton transitions are concealed beneath band-to-band transitions.

INTRODUCTION

The luminescence of self-trapped excitons (STEs) has been investigated vigorously in a wide range of crystals [1]. In many crystals the luminescence of triplet excitons is quenched at temperatures above the boiling point of liquid nitrogen. In some alkali halides, having a correlation between the exciton luminescence quenching and F -center formation, the activation energy determines the barrier between exciton states and the F , H pair. In other alkali halide crystals an energy barrier separates the excited and ground states of the excitons [1]. In alkaline-earth fluorides the triplet ($V_k + e$) state is unstable and relaxes into different ($F + H$) exciton states without activation energy [2].

For a long time it was assumed that several exciton luminescence bands in alkali halide crystals (σ bands with rapid quenching, about 10^{-1} sec, and π bands with slow quenching, about 10^{-3} sec), which are due to singlet and triplet excitons. With time it was perceived that singlet-triplet splitting is very small and cannot cause several new luminescence bands to form. Moreover, slow quenching components began to appear in the σ bands and rapid quenching components, in the π bands [3]. It became clear that the luminescence of both singlet and triplet excitons is often observed in each luminescence band.

Recently it has been demonstrated theoretically and experimentally that excitons in ionic crystals have several minima on the surface of the adiabatic potential, which corresponds to several possible ionic configurations [1]. Besides the "classic" $V_k + e$ exciton or on-center configuration, there are also two off-center configurations. One of them is called a weakly displaced (weak off-center) configuration and the other, a displaced (off-center) configuration. The basis of such models of excitons were the magnitude of the Stokes shift of the exciton luminescence band [3] and the energy of the absorption band of the electronic component of the excitons [4]. Undisplaced and displaced configurations differ as to vibrational frequencies of the hole component of the exciton (close to the frequencies of V_k and H centers) in the resonance Raman scattering spectra [5].

Self-trapped excitons in fluoride crystals with the cubic perovskite structure ($KMgF_3$, $RbMgF_3$) and with the tetragonal scheelite structure ($LiYF_4$) were studied by the method of optical detection of ESR [2]. Self-trapped holes were also detected in those crystals.

In this review we generalize the results of studies of excitons in some low-symmetry fluoride crystals, barium fluorohalides and lanthanide trifluorides, which are of practical interest. Barium fluorohalide crystals are used as storage screens [6] and lanthanide trifluoride crystals are very promising as scintillators [7].

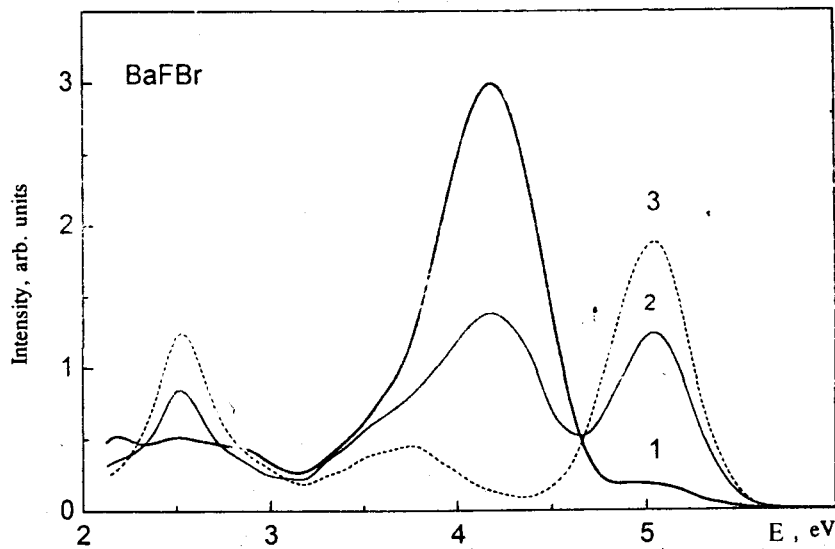


Fig. 1. Luminescence spectra of BaFBr crystals under excitation with 7.7-eV photons at different temperatures, K: 1) 78.5, 2) 62, 3) 17.3.

Excitons in Barium Fluorohalide Crystals

A 3.25-eV ($V_k + e$) luminescence band was observed in BaFCl crystals after x-irradiation upon illumination in the F band at 77 K [8]. A similar band at 3.3 eV was observed upon excitation in the BaFCl exciton absorption band [9, 12]. A 4.3-eV band was observed in BaFBr upon excitation in the exciton absorption band [10]. A luminescence band at about 5.1 eV in BaFBr also belongs to excitons [12, 13].

Two types of triplet excitons were detected in barium fluorohalide crystals [12]. Excitons of one type are transformed into the other type at 20-40 K in BaFCl and 60-80 K in BaFBr. In BaFBr crystals they have different luminescence bands at 4.2 and 5.15 eV, while in BaFCl they differ only as to quenching times. That the two luminescence bands in BaFBr belong to different types of triplet excitons was also established in a parallel study by Ohnishi, et al. [13]. They assumed there the excitons from the band at about 4.1 eV are due to perturbation by neighboring defects, possibly of the oxygen-vacancy type, which in the crystals studied were detected from an absorption band at about 5 eV. However, they did not detect a correlation between the intensity of the luminescence at 4.2 eV and the oxygen impurity. In the purest BaFBr crystals, in which impurity absorption was not observed, the transformation of the luminescence at 5.15 and 4.2 eV was the same as in crystals with oxygen impurity. We assume, therefore, that the 4.2-eV excitons are not linked to the impurity.

BaFBr. Luminescence bands at 5.15 and 4.2 eV were observed when crystals were illuminated in the Br-exciton band (Fig. 1). The 2.5-eV band in Fig. 1 is due to oxygen-vacancy centers [9] and the 3.7-eV band, to the background impurity. Both bands were also observed under excitation with 7.0-eV photons but the 4.2- and 5.15-eV bands were absent. The relation between the exciton bands depends on the temperature. The intensity of the 5.15-eV band increases as the temperature is lowered while that of the 4.2-eV band decreases. The temperature dependence of the normalized intensities of both bands clearly indicates transformation of one band into another and does not depend on the oxygen impurity or on excitons of different types. For a thermally activated transformation we can write [1]

$$I = I_0 / (1 - A \exp(-E/\kappa T)), \quad (1)$$

where E is the potential barrier to the transformation, $A = t_r/t_n$ is the ratio of the radiation and radiationless lifetimes. The experimental data are consistent with the formula for $E = 0.064$ eV and $A = 1.4 \cdot 10^5$. If the 4.2-eV band arises from the 5.15 eV-band, we can write

$$I(4,2 \text{ eV})/S = 1 - I(5,15 \text{ eV})/S. \quad (2)$$

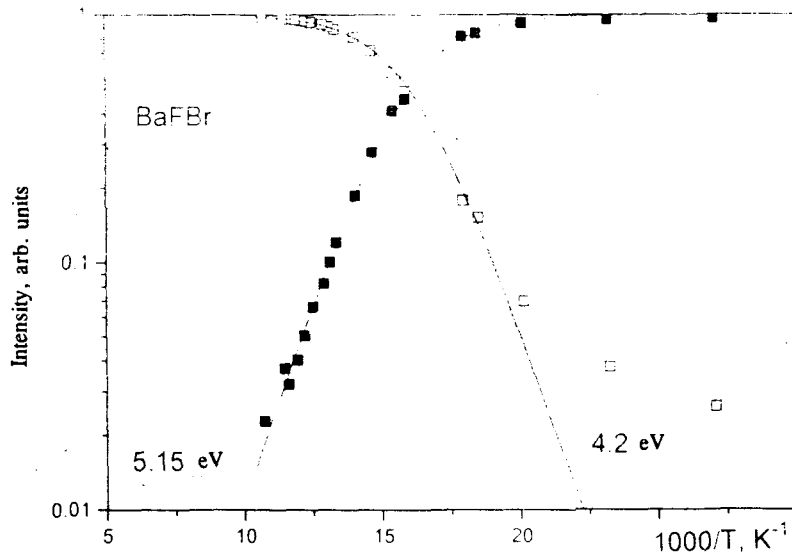


Fig. 2. Temperature dependence of the intensity of exciton photoluminescence in BaFBr under 7.7-eV excitation. The intensities of the bands have been normalized to their sum. The solid curves were calculated using Eqs. (1) and (2) (see text).

As is seen from Fig. 2, that assumption is correct. Slightly different parameters (0.118 eV and $2.4 \cdot 10^7$) were determined in [13].

Both exciton bands are also observed under excitation by x-rays and photostimulated recombination of electrons from *F* centers with self-trapped holes and have the same temperature dependence.

BaFCl. Only one luminescence band associated with excitons was observed in BaFCl crystals, in contrast to BaFBr. That band was observed under excitation with photons with an energy greater than 8 eV, x-rays, and ($V_k + e$) photostimulation. With rising temperature the intensity of the band roughly doubles in the interval 20-50 K. The quenching time of the luminescence decreases and becomes constant above 30 K. This behavior of the lifetime is very unusual. It can be explained by thermally activated transformation of one kind of excitons into the other kind, with a different lifetime. The luminescence intensity of the second kind of excitons can be described as

$$I_2 = I_{20} (1 - I_1/I_{10}). \quad (3)$$

The parameters obtained were $E = 0.017$ eV and $A = 200$.

From those assumptions we find that the quenching time of low-temperature exciton luminescence is equal to the lifetime of excitons of the first kind. At temperatures above 50 K the luminescence quenching time is determined by the lifetime of excitons of the second kind. Luminescence quenching at temperatures between 20 and 50 K should consist of two components in the absence of interaction between the levels or one component with an intermediate quenching time when there is thermal equilibrium between the levels. The experimental data indicate thermal equilibrium between different times of excitons.

Quenching of Exciton Luminescence in BaFBr. The quenching of luminescence of the 4.2- and 5.15-eV exciton bands in BaFBr, which are caused by the excitation of a crystal in the exciton absorption band (7.5 eV), has been studied in detail [14]. The quenching of 5.15-eV luminescence is exponential. Above 50 K the quenching time decreases in proportion to the decrease in the integrated intensity of that band. The kinetics of 4.2-eV luminescence consists of initiation and quenching stages. The initiation time increases from 0.1 to 200 μ sec at the temperature is lowered from 100 to 60 K. The quenching of luminescence at 4.2 eV is constant at 7 μ sec in this temperature interval. The results are explained well by a simple model with two minima and an excited triplet state. The potential barrier between the minima, which is determined from the temperature dependence of the 4.2-eV luminescence rise time is 47 MeV [14], which is slightly smaller than the barrier as determined from the temperature dependence of the steady-state luminescence.

Discussion. The results indicate that in barium fluorohalide crystals (BaFCl, BaFBr) excitons have two configurations, separated by a potential barrier. Recombinations of those configurations lead to spectrally inseparable luminescences in BaFCl

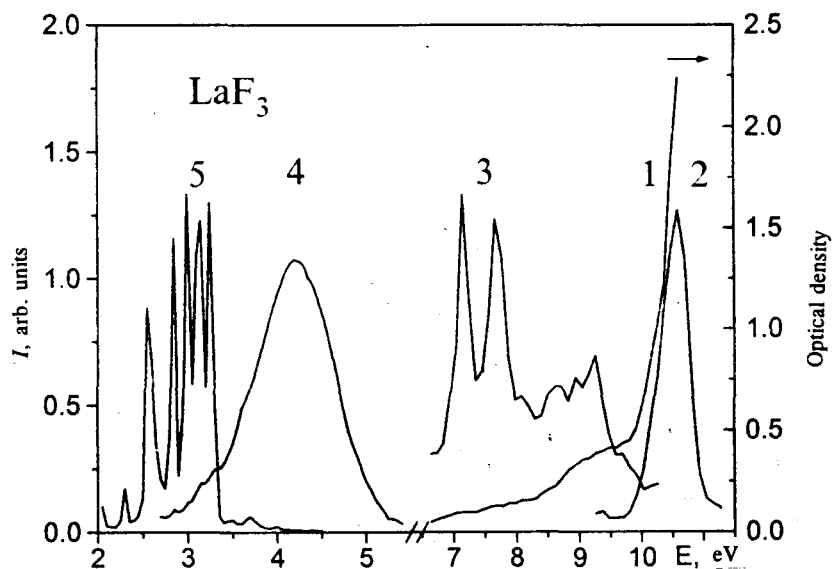


Fig. 3. Absorption (1), excitation (2, 3), and luminescence (4, 5) spectra of LaF_3 crystals, measured at 295 (1), 78 (3, 5), and 16 K (2, 4).

with a small potential barrier (0.017 eV) and to spectrally separated luminescence bands in BaFBr with a relatively large potential barrier (0.05-0.06 eV).

Crystals of alkaline-earth fluorides at helium temperatures were observed to have several luminescence quenching components [15], which are associated with excitons of different configurations (vacancy in the nearest-neighbor and subsequent sites). In alkaline-halide crystals at least two configurations of triplet excitons with different localization of an anion vacancy. The potential barrier between them is 10-100 MeV. Emission does not occur from the high-temperature configuration with vacancy removed. Moreover, three exciton configurations are possible for the nearest-neighbor location of the vacancy: on-center and two off-center, compact and noncompact [17].

Energy relaxation of Br_2 -excitons in BaFBr was calculated in [18, 19]. Relaxation along the (100) axis and the out-of-plane relaxation (roughly along (111)) was considered. In both cases the energy stabilization was 0.5-1.2 eV. A potential barrier of several tens of electron volts was detected for motion along (100) [18, 19]. The experimental results are in agreement with those calculations. The difference between the energies of two exciton bands (about 1 eV) can be considered to be the stabilization energy. The measured potential barrier (less than 0.1 eV) is also in reasonable agreement with the calculated value.

Low-temperature excitons in BaFBr and BaFCl are presumably associated with the on-center configuration and high-temperature excitons, with the off-center configuration [12]. The results of theoretical calculations [18, 19] point to the possibility of off-center excitons existing in BaFBr .

The exciton luminescence bands are divided into three groups in regard to the Stokes shift. A shift of about 0.3 Ex (Ex is the energy of the long-wavelength exciton absorption band) is characteristic of on-center excitons and 0.6 Ex, of off-center excitons. An intermediate Stokes shift is specific to weak off-center excitons [2]. Using that criterion, we assume that 5.15-eV excitons in BaFBr are on-center excitons and 4.3-eV excitons are weak off-center excitons. Excitons from the luminescence band at about 5.0 eV were also classified as on-center excitons in [13]. In BaFCl crystals both types of excitons evidently are off-center.

At present it is difficult to make more definite conclusions about the nature of two exciton configurations in barium fluorohalides.

Excitons in the Lanthanide Trifluoride Crystals LaF_3 and CeF_3

Despite the simple chemical composition of lanthanide trifluorides, the properties of excitons and other radiation defects in those materials have been studied very little. For many ionic crystals self-trapping of excitons is accompanied by self-trapping of holes. Self-trapped holes were detected recently in LaF_3 crystals [21]. The broad luminescence band with maximum

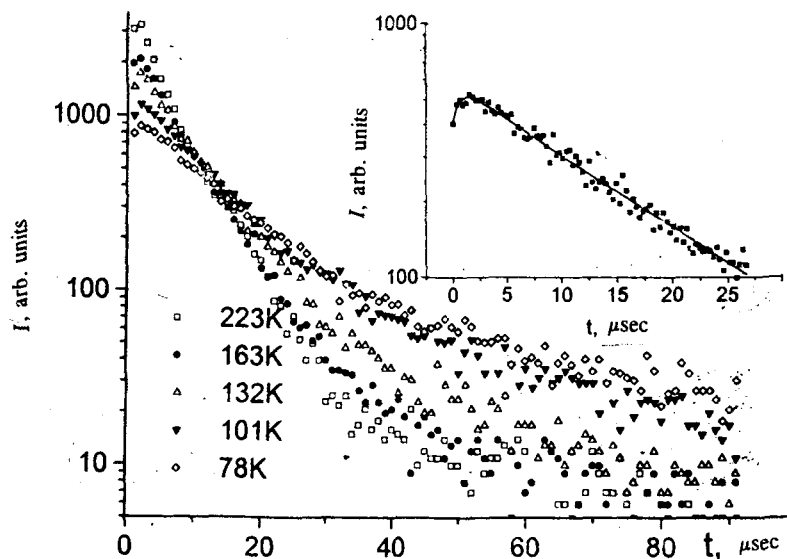


Fig. 4. Quenching of exciton luminescence (4.1-eV band) in LaF_3 under excitation with 10.5-eV photons. Inset: kinetics of exciton luminescence in LaF_3 at 78 K. The curve was calculated with allowance for the exponential initiation and quenching components (see text).

at about 340 nm is assumed to belong to self-trapped excitons [22]. This band was observed under excitation with x-rays and with 20-eV photons [21, 22]. A band at about 4 eV predominates in the x-ray luminescence spectrum below 220 K and that band is assumed to belong to the cerium impurity present in crystals at the level of several ppm [21].

Early studies on trifluorides, using synchrotron radiation in reflection spectra, did not detect a peak that could belong to excitons [26]. The reflection spectra indicated strong band-to-band transitions in the region 10-15 eV, principally from the $F-2p$ valence band to the $5d$ and $6s$ conduction band of lanthanides [26]. All of the features of the reflection peaks at 10-15 eV in polarized light were interpreted in terms of band-to-band transitions.

The lack of a strong, distinct exciton absorption peak was observed in LaCl_3 and LaBr_3 thin films, although a weak, indistinct band with an absorption coefficient of about 10^5 cm^{-1} was observed in chlorides at liquid-nitrogen temperature [20]. The width of the observed spectra suggests that band-to-band transitions dominate over exciton transitions [20].

Excitons usually absorb light in the region below band-to-band transitions, which begin from 10.5 eV for lanthanide trifluorides. Accordingly, we studied the luminescence of pure crystals under excitation by light in the region near band-to-band transitions at 9-12 eV.

Experimental Procedure. Crystals of LaF_3 and CeF_3 were grown by the Stockbarger method. Oxygen was removed by introducing 1-3 wt. % PbF_2 into the stock. The mixture was slowly heated in a vacuum until it melted, with holds at 400, 800, and 1200°C. The crystals were grown in a vacuum of 10^{-3} - 10^{-4} torr. Vacuum ultraviolet transmission served as a measure of the purity of the crystal. The LaF_3 crystals with the best ultraviolet transmission were grown from special-purity raw material, prepared at the Angara Electrolytic Chemical Works. Another crystal with such good transparency was kindly supplied by R. T. Williams. That crystal was grown by the Optovac company from raw material prepared from 99.999% pure lanthanum oxide [21]. Under excitation above 10 eV both crystals exhibited an identical luminescence band at 4.1 eV, but had different luminescence line spectra under excitation with photons of lower energy. Obviously, those lines are due to $5d_6, 0-4f$ transitions in impurities of rare-earth ions, the concentration of which has been estimated to be several ppm. The thickness of the crystals was 2-4 mm.

The absorption spectra of trifluorides were measured with a VMR2 vacuum monochromator. The luminescence was recorded with an MDR2 diffraction monochromator or through a UFS2 filter. The luminescence quenching was measured by the single-photon method, using a time-to-number converter. The flash lamp was filled with argon at a pressure of 1-3 atm.

Results. A broad luminescence band at about 4.1 eV was observed in all LaF_3 crystals under excitation in the region 9.8-11 eV (excitation peak at about 10.5 eV) (Fig. 3). The luminescence band was slightly asymmetric and the low-energy edge was slightly broader. The luminescence yield at 78 K was about 100%.

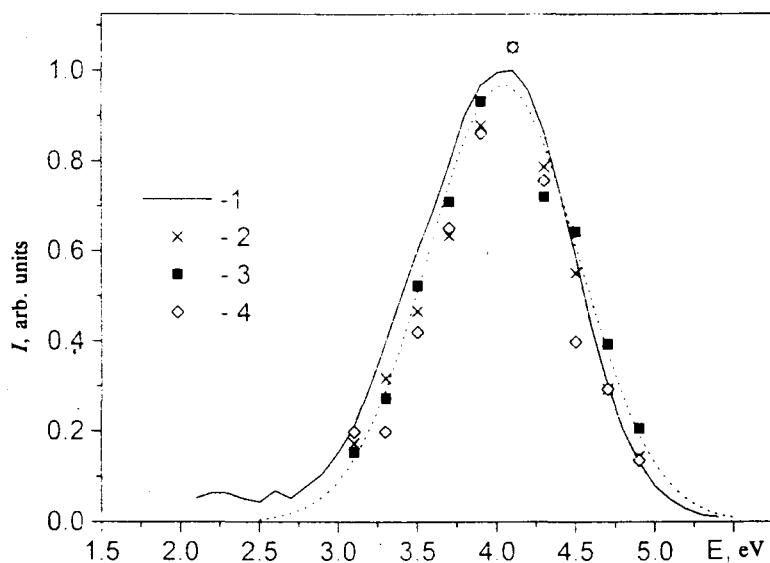


Fig. 5. Luminescence spectra at various stages of quenching: 1) steady-state luminescence, 2) 1 μ sec, 3) 30 μ sec, and 4) 50 μ sec after a pulse. The dotted line indicates the Gaussian shape of the luminescence band.

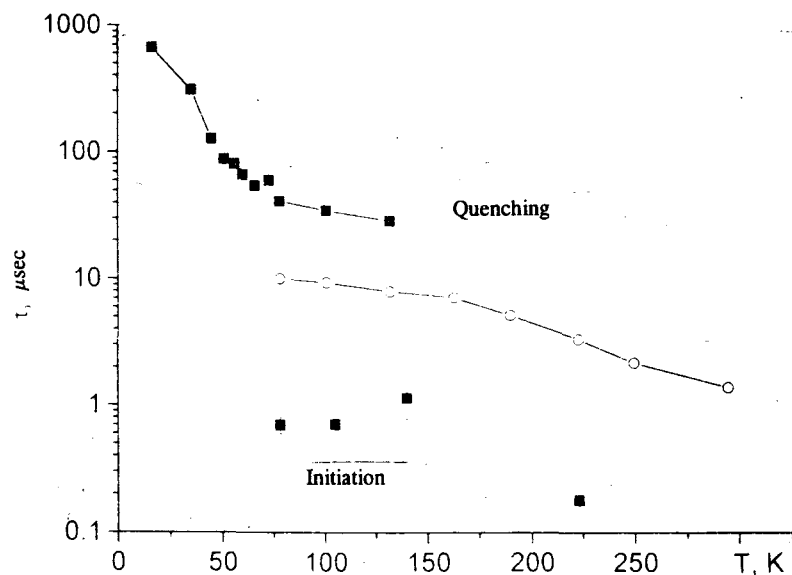


Fig. 6. Temperature dependence of two quenching components and the initiation component of exciton luminescence in LaF_3 .

Luminescence line spectra were observed below 9.8 eV. Their shape depends on the purity of the initial material and is due to rare-earth ion impurities. In crystals of lower purity an anticorrelation was observed between the impurity and 4.1-eV luminescence excitation spectra in the region 9-10 eV.

The absorption spectrum of pure LaF_3 crystals at room temperature exhibits a strong growth of absorption in the region above 10 eV. A distinct band with a maximum at 10.5 eV and a half-width of 0.6 eV at 78 K is observed in the excitation spectrum of 4.1-eV luminescence (see Fig. 3) The width of the excitation band is unusually small. At about 11 eV the excitation efficiency drops to a low value. Usually the exciton excitation spectrum has a long tail, which lies above the first exciton peak [2] and extends into the region of band-to band transitions.

When the temperature was lowered from room temperature to 78 K the ultraviolet band intensity increased several-fold with a 0.15-eV short-wavelength shift of the maximum; the excitation band also shifted by 0.1 eV. No higher-energy luminescence bands under x-ray excitation at 80 K were observed in the luminescence spectrum up to energies of 9 eV.

The 4.1-eV luminescence is characterized by long quenching in the millisecond range (Fig. 4). No shorter components were observed. The quenching time increased from 6 μ sec at 290 K to 600 μ sec at 12 K. The quenching time does not depend on the exciting photon energy. The spectra of steady-state luminescence and luminescence in both quenching components are the same (Fig. 5). Despite the asymmetry of the 4.1-eV band, the quenching time at 78 K did not vary within the luminescence band. In the temperature interval 80-150 K we observed two similar quenching time components (Fig. 6).

The luminescence kinetics has a stage of initiation of 4.1-eV luminescence with a characteristic time of about 1 μ sec (see inset to Fig. 4). The initiation time does not depend on the temperature in the region 78-140 K, at least, and the quenching time decreases from 15 to 9 μ sec. The initiation time also decreases above 140 K (Fig. 6).

CeF₃. The luminescence spectra of CeF₃ crystals exhibit distinct bands at 4.1 and 4.3 eV (that belong to 5*d*–4*f* transitions in cerium ions) as well as a broad band at 3.5 eV under excitation in the region 5-11 eV at 78 K. Other bands did not appear under excitation in the region 10-10.5 eV.

The quenching time is about 20 nsec for the allowed 5*d*–4*f* transitions in cerium ions [23]. Slow quenching components with a microsecond length appeared above 7 eV. Similar results were observed earlier [23]. Just as for steady-state luminescence new components were not observed in the quenching of cerium luminescence above 9.5 eV, which could be attributed to fluoride excitons.

DISCUSSION

X-Ray Excitation. It is extremely interesting to compare the temperature dependence of LaF₃ luminescence under x-ray and ultraviolet excitation. As is assumed, the 5*d*–4*f* transitions in the cerium impurity with forbidden spin-orbit splitting at about 0.25 eV is the most intensive part of the spectrum of 280 to 305 nm (4-4.4 eV) [25]. On the other hand, as follows from the data of [25], the band at about 290 nm (4.3 eV) grows relative to the other impurity bands at 360 and 490 nm as the temperature decreases. The last band evidently belongs to the praseodymium impurity [25]. Such behavior is characteristic of exciton luminescence, which is the main luminescence at low temperatures, while at higher temperatures excitons transfer energy to the impurities [2]. We assume, therefore, that the broad ultraviolet band observed in [25] more likely belongs to excitons rather than the cerium impurity.

The band at 290 nm is very weak at room temperature, becomes stronger as the temperature rises, and reaches a maximum at 150 K. The temperature of the maximum corresponds to the largest of the two thermoluminescence peaks [25]. Clearly, both the thermoluminescence and photoluminescence peaks are due to charge carriers (possibly holes) being freed. In our experiments the 4.1-eV luminescence increases constantly from 290 K to 78 K. The difference in the temperature dependences of x-ray luminescence and photoluminescence means that primarily excitons and not electrons and holes are formed under photon excitation.

Initiation of Luminescence. Luminescence quenching is often used to obtain important information about transition probabilities and the structure of lower excited states. The luminescence initiation stage can give information about the mechanism by which the excited state is populated. Usually the population of the luminescent state of triplet excitons is a very rapid process in the picosecond range. Nevertheless, in some cases the initiation time may be fairly long. A long stage of growth of exciton luminescence was observed in low-symmetry BaFBr and LaF₃ crystals.

The luminescence kinetics can be described in general in terms of exponential initiation and exponential quenching. With some minor assumptions, taking only one initiation stage and one quenching stage into account, we can write

$$I = I_1 \cdot \exp(-t/\tau_3) \cdot [1 - I_2 \cdot \exp(-t/\tau_p)], \quad (4)$$

where I_1 and I_2 are initial intensities. The first factor on the right side of the equation describes the initial intensity while the second and third describe the luminescence initiation and quenching. For the model to be simple I_2 should be 1. The kinetics often incorporates a very fast initiation stage followed by a slow stage. This can be described formally by introducing a value $I_2 < 1$. The calculated curves are in fair agreement with the experimental curves for $I_2 \approx 0.3$ (see Fig. 4).

The lack of a temperature dependence of initiation at low temperatures may be due to tunnel transitions, when transitions through the barrier begin above 140 K. The physical nature of such a barrier may be a barrier between two exciton configurations, as was observed in cases with BaFBr. The lack of low-temperature quenching of 4.1-eV luminescence and the absence of a second luminescence band, however, make this assumption unlikely. Another possible cause of the long initiation

time may be a barrier to exciton self-trapping. The best-known self-trapping barrier is 30-40 MeV [2]. In the given case it is substantially higher. And there is almost no impurity luminescence in the low-temperature x-ray luminescence spectra of LaF₃ [21]. Impurity luminescence should be observed when a barrier to self-trapping exists and, consequently, the exciton mean free path to self-trapping is long. The nature of the initiation of exciton luminescence in LaF₃, therefore, is an open question.

CeF₃. The absence of fluoride excitons (which are formed under excitation of an electron from the 2*p* band of fluorides) correlates with the absence of V_k centers in those crystals. Stable V_k centers were not detected at 78 K in either the ESR spectra [21] or the optical absorption spectra [24].

Transitive Absorption. An attempt was made to detect transitive absorption of excitons in LaF₃ and CeF₃ crystals [25]. The strong absorption observed in LaF₃ and CeF₃ 0.5 μsec or longer after an electron pulse at temperatures of 10-570 K did not differ from the steady-state absorption spectra. These results indicate that excitons have a considerable quenching time and should be visible in transitive absorption spectra. Excitons are formed in LaF₃ by an electron beam less efficiently, therefore, than are *F* centers and other radiation defects.

In all likelihood the primary radiation defects in LaF₃ and CeF₃ are formed by the trapping of band electrons in existing anion vacancies and self-trapping of holes and not by exciton decay, as in many crystal. It is not yet entirely clear whether those vacancies are intrinsic.

Urbach Absorption Edge. In many materials the low-energy tail of the exciton absorption band is an exponential function of the photon energy. Often a straight line in semilogarithmic coordinates obeys the empirical Urbach – Toedzawa rule

$$a(E) = a_0 \exp(-\sigma(E_0 - E)/\kappa T). \quad (5)$$

The family of straight lines (in semilogarithmic coordinates), measured at different temperatures, converge at one point, which determines the energy E_0 . The empirical coefficient σ is an important characteristic of exciton – photon interaction. The small value of σ_0 (high-temperature limit of σ) is proof of the self-trapping of excitons [2]. This rule is also valid for silver halides, where no strong exciton absorption peak is observed, because of indirect transitions.

The fundamental absorption edge in wide-gap glasses obeys the modified Urbach rule [28]

$$a(E) = a_0 \exp(AE + T/T_1), \quad (6)$$

where A is a constant that characterizes the slope of the absorption line and T_1 is a temperature. The main difference from the "crystal" absorption edge is that the absorption lines at various temperatures (in semilogarithmic coordinates) are parallel. The slope of the absorption line is several times smaller than in crystals, the absorption constant A for a series of glasses lies in the range 5-6 eV⁻¹, and $T_1 = 200-250$ K [28]. One cause of the "glassy" fundamental absorption edge evidently is the "smearing" of the band edges because of the disordered nature of the structure (absence of long-range order) and the appearance of self-trapped states [28].

The LaF₃ absorption edge is very unusual. The absorption consists of two parts. The first does not depend on the temperature and is characterized by a slope $A = 3$ eV⁻¹. The second part is temperature-dependent. Absorption at various temperatures is a family of parallel curves with $A = 5.4$ eV⁻¹ and $T_1 = 256$ K.

This "glassy" absorption is possibly caused by the "softness" of the fluoride sublattice and some disorder in their arrangement. Fluoride vacancies have a very low migration energy, about 0.1-0.2 eV. A study of the NMR spectra of ¹⁹F atoms in lanthanide trifluorides led to the conclusion that the fluorine atoms are distributed randomly among the locations, the number of which is twice that of atoms [29]. At about 0°C instead of several lines we observe only one; it corresponds to the signal of ¹⁹F nuclei, which diffuse rapidly through the locations of the fluorine sites in mixed layers (F(3) position of fluorides). Near 150°C two lines of atoms in fluorine layers (F(1) and F(2) fluorine positions) also merge into one, which corresponds to the process of rapid exchange between them [29].

Let us summarize all the properties of 4.1-eV luminescence in LaF₃ crystals, which support its exciton nature:

- luminescence is detected in all LaF₃ crystals, indicating that the observed luminescence is more likely intrinsic rather extrinsic:
- luminescence is excited by photons with an energy that is comparable with the magnitude of the band-to-band transitions, much like excitons in other crystals; and
- the quenching time is in the microsecond range. Such a quenching time is typical of triplet excitons. The temperature dependence is similar to that for excitons and alkaline-earth fluorides.

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