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Luminescence Due to Radiative Transitions between Valence Band and Upper Core Band in Ionic Crystals (Crossluminescence)

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In some wide band gap halides of heavy alkali and alkaline-earth metals (BaF_2 , CsCl , RbF etc.) the energy separation between the valence band involving mainly the halogen electronic states and the upper cation core band is smaller than the band gap. Under the excitation generating holes in the core band radiative electronic transitions from the valence band to the core band take place giving rise to a specific kind of intrinsic emission which is proposed to call crossluminescence. Its decay time is about 1 ns and the thermal quenching starts at temperatures well above room temperature. The width of the emission spectrum practically coincides with the width of the valence band deduced from ultraviolet photoelectron spectroscopy and the shape of the spectrum depicts the electronic structure of the valence band.

In einigen Alkali- und Erd-Alkalihalogeniden (BaF_2 , CsCl , RbF u. a.) ist die Energiedifferenz zwischen dem Valenzband und dem höchsten Atomrumpfband kleiner als die Energielücke. Unter hochenergetischer Strahlungsanregung, die Löcher im Atomrumpfband generiert, treten strahlende elektronische Übergänge von Valenzband zum Atomrumpfband auf, eine spezifische Eigenlumineszenz, die „Crosslumineszenz“ genannt wird. Die Abklingzeit dieser Lumineszenz ist etwa 1 ns und die thermische Tilgung beginnt über Zimmertemperatur. Die Spektrumsbreite korreliert mit der Valenzbandbreite, wie durch Photoelektronenspektroskopie festgestellt wird, und die Struktur des Spektrums charakterisiert die Elektronenstruktur dieses Valenzbandes.

1. Introduction

The intrinsic luminescence of unactivated alkali halide and alkali-earth halide crystals has been the subject of numerous studies (see e.g. [1 to 5] and references therein). The most intense bands observed at low temperatures are due to the radiative decay of self-trapped excitons or to the radiative recombination of electrons with self-trapped holes at regular lattice sites (not involving any intrinsic defects or impurities). This luminescence can be excited with photons creating the lowest energy anion excitons or electron-hole pairs.

Besides this luminescence in BaF_2 another type of intrinsic emission²⁾ in the 200 to 230 nm region was observed with subnanosecond decay time and no thermal quenching at least up to 350 K [6, 7]. The nature of the CRL remained obscure until recently when its excitation spectrum was measured by Aleksandrov et al. using synchrotron radiation [8]. It was discovered that unlike practically all other types of intrinsic and extrinsic luminescence the CRL in BaF_2 cannot be excited with photons creating anion excitons and electron-hole pairs. The excitation threshold was found at 18 eV indicating that even the creation of the lowest energy cation (Ba^{2+}) excitons (reflection peak at 17.1 eV [9]) does not excite the CRL. The ultimate condition for the occurrence

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²⁾ To discriminate this type of luminescence we shall call it "crossluminescence" (CRL) on the grounds of its nature discussed later.

of this luminescence was found to be the presence of holes in the Ba^{2+} 5p core band leading to the conclusion that the luminescence is most likely due to radiative transitions of electrons from the F^- 2p valence band to the Ba^{2+} 5p band [8]. As the transitions between the bands formed by different ions in ionic crystals are called cross-transitions in X-ray spectroscopy [10] we propose the term “crossluminescence” (CRL) for this type of optical emission. We fully recognize the arbitrariness of the term “crossluminescence” as well as the notations of bands like “ F^- 2p band” — of course there is some contribution of covalence and the bands contain also some admixture of other electron states. Nevertheless in ionic crystals such “ionic approach” seems appropriate as convenient zeroth-order approximation.

After the publication of the excitation spectra of CRL in BaF_2 [8] we performed a thorough study of its emission spectrum in the whole transparency region and proposed its interpretation [11] based on the band structure calculations by Starostin et al. [12] and the experimental UPS data by Poole et al. [13] and Pong et al. [14]. In a short note [15] we described the CRL spectra of cesium halides as the result of radiative transitions between the valence bands and the Cs^+ 5p core bands.

The aims of this article are to give a more detailed analysis of some earlier published results and to present new experimental data on CRL in several simple and mixed halide crystals, to outline the generic features of CRL, and to formulate the main unsolved problems.

2. Experimental

The spectra and decay kinetics of the CRL were studied under excitation by an 7 keV electron beam with current density $\approx 1 \mu\text{A}/\text{cm}^2$ in stationary regime and $\approx 100 \mu\text{A}$ per cm^2 in the pulse regime. The experimental set-up based on a Seya-Namioka type vacuum monochromator with a concave diffraction grating (1200 grooves/mm) was used as described earlier [16]. The spectra were measured in a photon-counting regime using a FEU-106-type photomultiplier tube with a MgF_2 entrance window. The decay kinetics were studied using the correlated photon-counting method under excitation with 100 ns long electron pulses with decay time 2 ns which was also the limit of the minimum measurable CRL decay times.

The fluoride crystals were grown by the Bridgman method in graphite crucibles in fluorizing or inert atmosphere. The chlorides and bromides were grown in fused silica crucibles in air. For CRL measurements small samples (about $1 \times 1 \times 0.5 \text{ mm}^3$) were fixed to the cryostat's cold-finger using indium metal.

3. Results and Discussion

3.1 BaF_2 crystals

To obtain the luminescence component with short decay time the cathodoluminescence spectra of BaF_2 were measured in a 40 ns strobe during the 100 ns excitation pulse. In the 5 to 7.5 eV range only the short component with decay time < 2 ns is observed (Fig. 1), at smaller energies of quanta the component with about 600 ns decay time is also observed.

Before the analysis of the CRL spectra of BaF_2 let us have a general view on the transitions between two nearly filled bands. In the case of direct transitions (not involving phonons) the emission spectrum can be presented as

$$I(\hbar\omega) = \sum_{k_1, k_2} P_{k_1, k_2} Q_{k_1, k_2} A_{k_1, k_2} \delta(E_{k_2} - E_{k_1} - \hbar\omega),$$

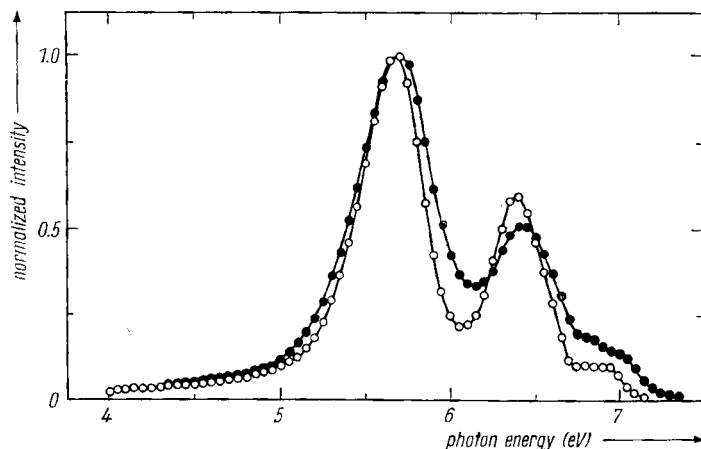


Fig. 1. Cathodoluminescence spectra of BaF_2 measured in 40 ns strobe during the exciting pulse at $T = 80$ (○) and 300 K (●)

where P_{k_1, k_2} is the joint density of states in the two bands, ϱ_{k_1} the distribution of holes in the lower band, A_{k_1, k_2} the transition probability between the states of the two bands, and δ the delta function.

Consequently the emission spectrum in principle can span from the energy $(E_{k_2, \min} - E_{k_1, \max})$ to $(E_{k_2, \max} - E_{k_1, \min})$, i.e. the width of the spectrum can equal the sum of both involved bands. The distribution of intensity within this range of energy is determined by the members characterizing the band structure (P_{k_1, k_2} , A_{k_1, k_2}) as well as by the distribution function of holes in the lower band at the moment of photo-transition³). The latter, in turn, is determined by the excitation parameters and the thermal relaxation process of the holes. In a particular case the holes can be created in the upper part of the lower band by optical excitation with photons with energy just above the photoionization threshold of this band. In all other cases — excitation with photons of higher energy or with charged particles — the holes are generated with some probability throughout the lower band and the emission spectrum is determined by the two competing processes, the thermal relaxation of the holes within the lower band and their phototransitions to the upper band.

With these considerations in mind let us now correlate our results on BaF_2 CRL spectra with the experimental UPS data [13, 14] and the theoretical analysis of the band structure [12]. In Table 1 the ionization thresholds and the widths of the valence band

Table 1

UPS data on the band structure and the parameters of the CRL spectrum of BaF_2 (eV)

	[13]	[14]	this work
threshold of F^- 2p valence band	11.0 ± 0.1	10.7 ± 0.2	
threshold of Ba^{2+} 5p core band	18.2 ± 0.1	18.0 ± 0.2	
difference of threshold energies	7.2 ± 0.1	7.3 ± 0.2	
width of the valence band	3.4 ± 0.1	2.9 ± 0.2	
width of the core band		4.2 ± 0.2	
maximum energy of CRL photons			7.3 ± 0.1
width of the CRL spectrum			3.3 ± 0.2

³) We can neglect the presence of holes in the upper band at low excitation intensities.

and the Ba^{2+} 5p core band are presented together with the width and maximum photon energy of the CRL spectrum. From the close coincidence of the maximum energy of CRL photons with the difference of the ionization thresholds it follows that at the moment of the phototransition the holes occupy only a narrow interval near the top of the Ba^{2+} 5p core band. If the holes would be more or less randomly distributed over the Ba^{2+} 5p core band the maximum energy of CRL could reach 11.5 eV, i.e. exceed the energy of the BaF_2 absorption edge with consequences to be discussed below. The fact that the emission intensity at 8.0 eV is at least three orders of magnitude smaller than at 5.6 eV under excitation with 7 keV electrons indicates, in our opinion, that the process of hole relaxation to the top of the core band has been finished before the transitions giving rise to CRL take place and that consequently the probability of phototransitions involving hot holes is much smaller than that of relaxed holes.

The problem of polarization deserves more detailed analysis — it seems rather a result of coincidence that the maximum energy of CRL photons nearly coincides with the difference in ionization energy thresholds of the involved bands. The point is that in UPS the energies of unrelaxed states in both bands are determined whereas in CRL the transition takes place after the vibrational relaxation has ended and the polarization around the hole in the Ba^{2+} 5p band has taken away some energy and consequently some “Stoke’s shift” is anticipated. The absence of such a shift can be explained assuming that the polarization has shifted the levels in the F^- 2p band by approximately the same energy as those in the Ba^{2+} 5p band.

The close correspondence of the full width of the CRL spectrum to the width of the valence band (as determined from UPS measurements) indicates that the transitions involve states throughout the F^- 2p valence band. In contrast to the structureless nearly Gaussian shape of the valence band from UPS the CRL spectrum reveals at least four maxima of various intensities and shapes reflecting the density of states of the valence band multiplied by the transition probability function.

The band structure and density of states of BaF_2 has been calculated by Starostin et al. [12] (Fig. 2). The top of the Ba^{2+} 5p core band corresponds to the X-point in the Brillouin zone (BZ). The observed four maxima in the CRL spectrum can be attributed to the transitions from the four subbands in the F^- 2p valence band in the vicinity of the X-point. It should be noticed that the selection rules acting exactly at the X-point and forbidding two of the transitions in dipole approximation can change significantly when one goes away from this point. Unfortunately the very nature of the CRL excludes the possibility of a direct determination of the transition probabilities of separate transitions by measuring the decay times of separate CRL emission bands — the measured decay times of all transitions will be equal to the radiative decay time of the “fastest” transition because this transition will deplete the hole states in the core band precluding the observation of longer decay times. This consideration has gained experimental confirmation from the recent work of Kubota et al. [35], where the measured decay times of the two main CRL bands were determined to be exactly the same. So the transition probabilities of the separate CRL transitions are reflected not in their decay times but in the relative intensities of their bands which, unfortunately, are also determined by the density of states requiring independent high resolution measurements of UPS or some other methods to get finally the estimate of the transition probabilities of all bands.

The experimental results together with the electron energy band calculations support the interpretation of the subnanosecond luminescence of BaF_2 as the result of radiative transitions between the F^- 2p valence band and the Ba^{2+} 5p core band [8, 11, 35]. To gain more support to the concept of CRL we studied a number of other materials with analogous band structure.

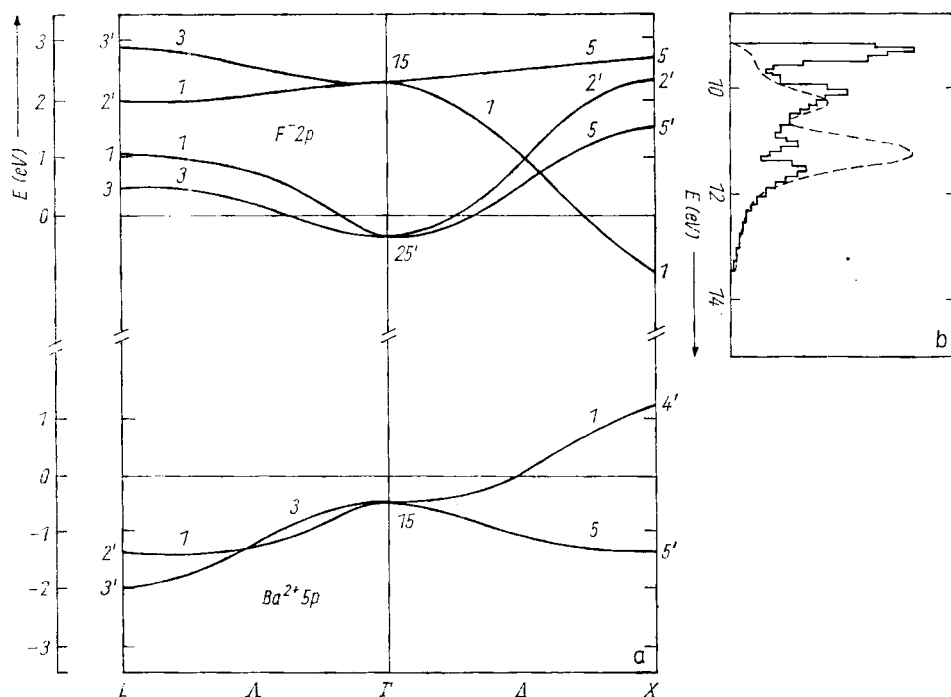


Fig. 2. a) Valence band and cation core band structure of BaF_2 [12]; b) valence band density of states [12] (—) and CRL spectrum of BaF_2 (---) normalized to equal width of the spectra

3.2 Cesium halides

As the ionization thresholds of the Cs^+ 5p core bands of cesium halides are lower than the thresholds of core bands of other alkali halides the CRL was anticipated in the region of relatively low photon energies. Fig. 3 presents the spectra of the fast com-

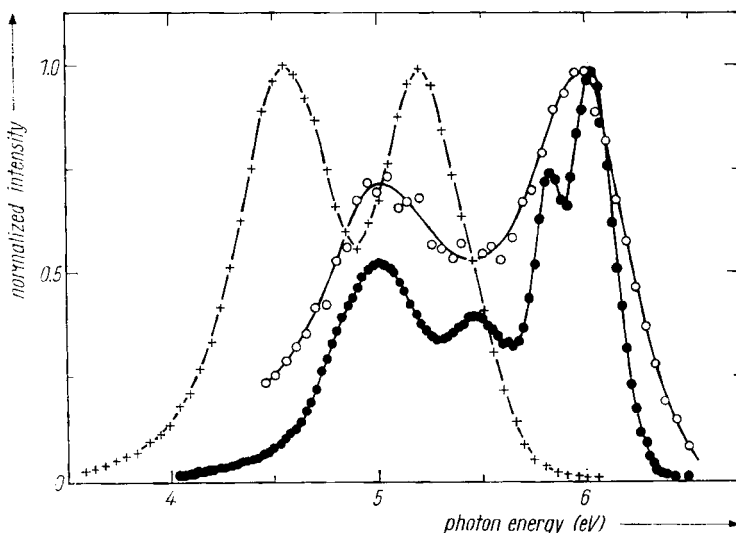


Fig. 3. Cathodoluminescence spectra of CsCl normalized to equal maximum intensity at 300 K (+) and CsBr at 300 K (○) and 80 K (●)

Table 2

UPS data on the band structure and the parameters of the CRL spectrum of cesium halides (eV)

	CsF	CsCl	CsBr	CsI
valence band threshold [17]	9.0 ± 0.2	7.9 ± 0.2	7.3 ± 0.2	6.5 ± 0.2
Cs ⁺ 5p band threshold [17]	13.3 ± 0.2	13.7 ± 0.2	13.9 ± 0.2	14.1 ± 0.2
difference of threshold energies	4.3	5.8	6.6	7.6
valence band width [17]	1.7 ± 0.3	1.8 ± 0.3	2.1 ± 0.3	2.4 ± 0.3
maximum energy of CRL photons	4.2 ± 0.1	5.6 ± 0.1	6.5 ± 0.1	
width of the CRL spectrum	1.9 ± 0.2	1.8 ± 0.2	2.0 ± 0.2	

ponent of the cathodoluminescence of two Cs halides. The main features of the spectra together with the UPS data [17] are summarized in Table 2. As the position of the Cs⁺ 5p core band is approximately the same in all crystals but the valence band ascends when going from fluoride to chloride and bromide the energy of CRL photons increases.

It should be noticed that the CRL of cesium halides was earlier observed by a number of authors [18 to 20], nevertheless the right interpretation could not be given because of the absence of excitation spectra. The recent measurements of the excitation spectrum of the CRL in CsBr [21] unambiguously confirmed the interpretation suggested in [15] — the excitation threshold (13.5 eV) corresponds to the ionization of the Cs⁺ 5p states giving rise to the CRL.

Using the data on CRL in Cs halides one can obviously analyze the criterion of the existence of CRL in materials with different band structure. In general, radiative electron transitions from the valence band to the nearest core band can take place whenever holes have been created in the core band. Such transitions were observed by Maiste et al. [22] in the ultrasoft X-ray emission spectra of LiF at about 45 eV where the strong intrinsic absorption precludes the emission from the bulk of the crystal. The highest CRL output can be (and really is) observed when the maximum energy of the CRL photons (practically the difference between the ionization thresholds of the corresponding bands) is less than the energy necessary to create the anion exciton⁴).

Such a situation is common to BaF₂, CsF, and CsCl in which intense CRL is observed in the whole temperature region under consideration. A previous study by Akerman [19] shows that the thermal quenching of CRL in CsCl starts above 800 K.

From the UPS data the eventual CRL transitions in CsI could be observed in the 5.2 to 7.8 eV region, which partially corresponds to the transparency region of the crystal (the first exciton peak is at 5.8 eV [24]). Nevertheless no fast-decaying emission with intensity exceeding 10⁻⁴ of that of CsCl under similar conditions could be observed in the 5.0 to 5.5 eV region. We attribute this to the possible role of Auger transitions from the upper part of the valence band leading to fast exhaustion of the holes in the core band. Such hypothesis renders also a plausible explanation to the peculiar temperature dependence of CRL in CsBr — here the CRL intensity decreases about 30 times when the temperature is increased from 80 to 300 K. Evidently the probability of non-radiative Auger-type transitions increases significantly as the result of the shift of the absorption edge and also of the "virtual" shift of the high energy edge of CRL

⁴) It should be taken into account that the energy of exciton in the vicinity of extra positive charge (hole in the core band) is about 0.5 eV smaller than that in the regular crystal [23].

with increasing temperature. It should be stressed here that the radiationless transitions have much higher transition probabilities — in the opposite case we should observe only a drop at the high energy side of the CRL spectrum corresponding to the increasing overlap with the absorption edge and no or a rather small drop of the transitions corresponding to the transparency region of the crystal.

Until recently there were no band structure calculations in Cs halides involving the Cs^+ 5p core band. In the paper of Satpathy [25] it has been shown that in CsCl the top of the Cs^+ 5p band corresponds to the X_7^- -symmetry and the Cl^- 3p valence band contains degenerate ($X_6^+ + X_7^+$) state and a lower X_6^+ -state. In accordance with this we observe two maxima in the CRL spectrum. In CsBr the three branches of the Br^- 4p band at the X-point are separated, thus giving rise to the three main maxima in the CsBr spectrum.

To gain additional confirmation to the concept of CRL it seemed useful to study the luminescence spectra of a number of solid solutions $\text{CsCl}_{1-x}\text{Br}_x$. It was anticipated that the introduction of Br^- ions into the CsCl crystals will give rise to electron states (impurity band) just above the top of the Cl^- 3p valence band resulting in additional CRL transitions on the high energy side of the CsCl CRL spectrum. Such transitions were actually observed in the region of about 6 eV where pure CsCl does not emit. The intensity of this emission was approximately proportional to the concentration of the Br^- ions. Unfortunately it was not possible to study in detail the emission at low Br^- concentrations corresponding to transitions from localized Br^- 4p states because of the overlapping emission of some radiation defects in the same energy range (see below). In the case of comparable molar fractions of CsCl and CsBr the CRL spectrum can be represented in the first approximation as the superposition of the spectra of the individual components reflecting the complexity and the increased total width of the valence band.

During the CRL measurements on CsCl at temperatures below 200 K an additional luminescence band at 6.0 eV was observed with intensity increasing with the irradiation time. Simultaneously the intensity of the main bands decreased and at a certain radiation dose the 6.0 eV band was the strongest one. The warm-up of the crystals above 200 K destroys the 6.0 eV band and restores the intensity of the main bands. We interpret this as the result of radiative transitions from some defect states above the valence band to the Cs^+ 5p band. The exact nature of the defect involved remains obscure because there are practically no data on CsCl radiation defects unstable at ambient temperature. The most probable candidate in our opinion could be the interstitial anion (I-centre) possibly stabilized by an alkali ion. It should be noticed that analogous transitions from defect states to core levels have been observed in X-ray emission spectra in some other materials (see e.g. [26] and references therein).

3.3 Rubidium halides and some other crystals

From the results of optical and UPS measurements of rubidium halides [24, 27] it follows that in RbF the whole CRL spectrum would correspond to the transparency region of the crystal and consequently the CRL intensity would be comparable to that in CsCl and CsF. The experiment confirmed the expectations (Fig. 4) — the two maxima of CRL at 5.4 and 6.1 eV are within the interval 5.2 to 6.8 eV where CRL could be anticipated from the band structure data of Inouye and Pong [27].

The band structure of RbF has been calculated by Kunz [28] providing the possibility to interpret the two observed maxima as the result of allowed transitions in the vicinity of the L-point from the L_2^- and L_3^- -states in the valence band to the degenerate L_1 , L_3 -state in the core band. As both transitions are fully allowed the strong difference of the intensities of both bands seems somewhat surprising as well as the change of the

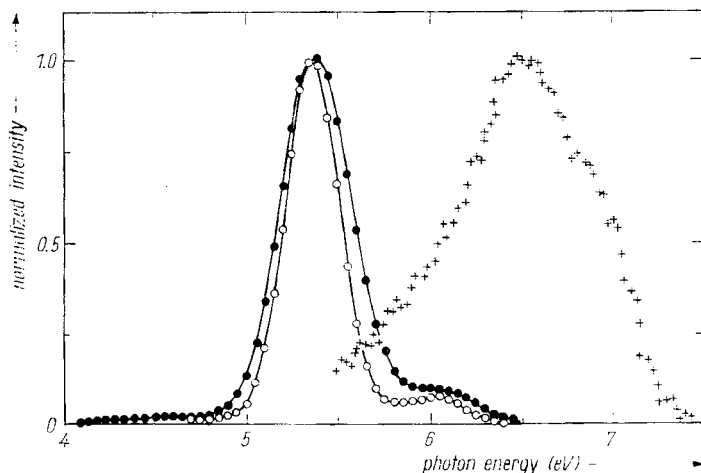


Fig. 4. Cathodoluminescence spectra of RbF normalized to equal maximum intensity at 80 (\circ) and 300 K (\bullet) and RbCl at 300 K (+)

intensity ratio with temperature. Unfortunately we do not have independent data on the density of states in both bands and the detailed shape of the core band. The latter determines the distribution of the thermalized (relaxed) holes in this band which influences the distribution of transitions in the vicinity of the L-point in the BZ.

In RbCl the eventual CRL transitions could be in the 6.9 to 8.5 eV region [27] which is significantly overlapped by the intrinsic absorption (the first exciton peak is at 7.4 eV [24]). Because of this the CRL in RbCl is by more than three orders of magnitude weaker than in RbF. In LaF_3 also the electronic energy band structure [29] prevents the transformation of a significant part of the energy deposited as holes in the La^{3+} 5p band into the CRL photons. As the band gap of this material is > 10 eV a weak CRL is observed in the energy range 6 to 9.5 eV.

From general considerations we anticipated that the CRL spectrum in BaY_2F_8 should be in the same spectral range as that of BaF_2 . The experiment confirmed this hypothesis — relatively weak CRL is observed in the energy range 4 to 7.5 eV as one wide almost structureless band. The measurements are additionally hindered by the radiation damage of the sample by the exciting electron beam.

4. The Peculiarities of CRL as a Specific Kind of Intrinsic Emission and the Problems of Its Practical Applications

Although the mechanism of CRL has been intentionally studied hitherto very little the process itself has already found quite wide practical application in scintillation detectors (see e.g. [30 to 34] and references therein). BaF_2 and CsF have been proposed and studied as fast scintillators allowing to achieve high time resolution — 115 ps with BaF_2 crystals [33]. As the total light output of BaF_2 is about 40% of that of NaI(Tl) one can have also quite good energy resolution.

As the excitation of CRL requires the ionization of comparatively deep core energy levels its efficiency under excitation with high energy photons and particles is inherently smaller than that of the “conventional” recombination luminescence because of the smaller probability of ionization of core states by δ -electrons. It should be kept in mind that once we have created a hole in the core band we can get one CRL photon and one photon of “conventional” luminescence. If we assume that in BaF_2 any hole

in the F^- 2p band at LNT gives rise to one photon when recombination with a free electron takes place, and any hole in the Ba^{2+} 5p band gives one CRL photon when "jumping up" to the F^- 2p band, we get the ratio of hole production probability by γ -rays and fast electrons in the F^- 2p and Ba^{2+} 5p bands, respectively, as about 10:1 [11, 31]. As far as we know there are no direct measurements of the absolute CRL efficiency, nevertheless one can approximately estimate it as being about 1%.

Knowing the mechanism of CRL we can propose an explanation of one rather interesting experimental result — the fast component of the scintillation (CRL) in BaF_2 is strong under excitation with γ -rays, electrons, and also by fission fragments, but is practically absent under excitation with α -particles [32, 35]. The α -particles with energy < 10 MeV have relatively small velocities compared to the orbital velocities of core electrons and consequently the probability of ionization of the Ba^{2+} 5p core is small, so practically no CRL is observed. The fission fragments evidently do create holes in the Ba^{2+} 5p band and this can be the result of the rather high charge state of the highly energetic fission fragment as well as the "gathering" of the crystal electrons (including those from the Ba^{2+} 5p band) when the fission fragment stops at the end of its track.

To summarize let us formulate in general form the main peculiarities of CRL differentiating it from the other types of luminescence:

1. The CRL can be observed in some wide-gap ionic crystals as result of radiative electron transitions between the valence band and the upper core band. In particular cases localized electron states split off from these bands by intrinsic defects or impurities can also give rise to CRL.

2. The CRL can be excited only in processes creating holes in the energy band lying below the valence band. Therefore even under photoexcitation above threshold with high quantum efficiency the energy efficiency of CRL cannot exceed $\approx 50\%$, as inevitably a large part of the energy must be transferred to "conventional" luminescence or heat.

3. Opposite to the conventional luminescence where the elementary excitation usually can be regarded as a hole with one electron in a higher energy state in CRL the elementary excitation represents a hole with a continuum of filled band states above it. As a consequence the CRL is characterized by inverse population of energy states at any intensity of excitation and high transition probabilities (small decay-time constants). Another consequence is the absence of CRL transitions in photostimulated or thermostimulated processes, in other words, it is not possible to store the energy for CRL processes.

4. The CRL can be observed at ambient and higher temperatures (except some particular cases) allowing to use it in fast high-temperature scintillators.

The studies of CRL render new possibilities for the study of the valence band electronic structure with resolution exceeding that of UPS and XPS by more than an order of magnitude. In some cases the position of local states of intrinsic defects or impurities can be directly deduced from CRL measurements.

The CRL exploration has just started and many problems have not yet been solved. In particular measurements of the weak emission on the high-energy side of the CRL spectrum with high time resolution could give information on the hole relaxation processes in the core band. In materials with symmetry lower than cubic useful information could be obtained from polarization measurements of the CRL.

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