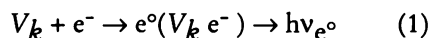


Chapter 1. Intrinsic Luminescence of Inorganic Fluorides

Introduction. Investigation of common scintillators involves studies of dopant centers (Tl, Na, Eu) which are introduced into the matrix (NaI, CsI). In recent times both investigators and practicing engineers have come to a conclusion that non-doped crystals of CsF, BaF₂, CeF₃, etc. can be used as scintillators. In such crystals there is no problem of a uniform even impurity distribution throughout the sample. Besides, pure compounds possess, as a rule, higher radiation hardnesses as compared to doped ones.

It is assumed in radiation physics of ionic crystals that intrinsic luminescence of a compound with a high (over 0.1 %) energy yield is due to excitonic luminescence [1.1]. When a crystal is excited by quanta or high energy particles it produces high energy carriers (electrons and holes), which, after a complicated process of energy exchange and subsequent thermalization, are transformed into low-energy electrons near the bottom of the conductivity band and holes near the upper valence band. The high yield of intrinsic luminescence of crystals is accounted for by a specific behaviour of the thermalized holes in compounds with a high degree of ionic bonding, alkali halides, in particular. In such compounds a hole of the valence band is located at two neighboring halides and forms a V_k centre within a very short time (about 10^{-12} sec). At a low temperature the V_k centre becomes a stable formation, normally, a self-trapped hole, and can act as a luminescence centre. The energy level in the forbidden band of the crystal corresponds to the V_k centre. This energy level is located at some distance from the top of the valence band, Fig. 1.1. *Thus, in a pure, i.e., free of doping centres, irradiated crystal a large number of luminescence centres, namely, V_k centres, are formed.*

Luminescence arises upon interaction of an electron (e^-) of the conducting band with a V_k centre. This luminescence has the same characteristics as the excitonic emission which arises upon optical formation of anionic excitons in the crystal. Therefore, we may assume that luminescence is emitted as a result of the reaction:



i.e., a relaxed exciton e° (at low temperatures - a self-trapped exciton STE) of the $V_k e^-$ type is formed, which then emits a quantum ($h\nu_{e^\circ}$) of light. The properties of excitonic luminescence were studied mainly on alkali halide crystals (AHC) [1.1 - 3]. These crystals had been used as model objects in solid state physics for quite a long time. Physical concepts worked out for AHC were then applied to other ionic crystals, including alkaline-earth fluorides, although it was not quite proper, as further studies showed.

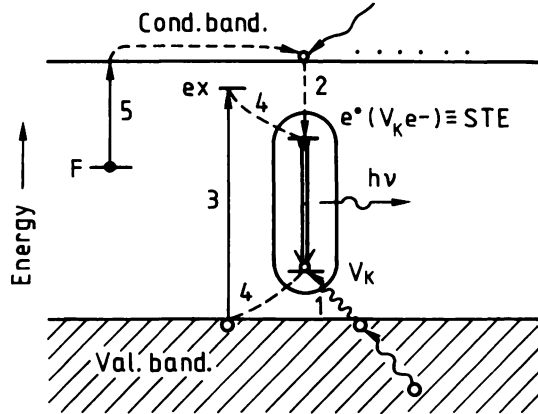


Fig. 1.1. Zone scheme of an ionic crystal which explains mechanism of excitonic luminescence:

- 1 - hole relaxation;
- 2 - electron entrapment;
- 3 - formation of an anionic exciton;
- 4 - relaxation of the exciton,
- 5 - photoexcitation

Intrinsic (excitonic) luminescence of AHC is effective at low temperatures only, when holes are self-trapped, i.e., V_k centres are immovable. Luminescence of AHC at room temperature has a low intensity, that is why it is hardly involved in the scintillation process. In alkaline-earth fluorides, i.e. in CaF_2 , SrF_2 , and BaF_2 , crystals, as well as in some other compounds the excitonic luminescence retains a high yield at room temperature. In this case one can speak about involvement of metastable delocalized V_k centres in the reaction (1). The metastable V_k centres that exist in the radiation field vanish after emittance of V_k -excitons and the sample regains its initial properties.

Alkaline-earth fluorides (AEF), particularly CaF_2 , and SrF_2 crystals were studied primarily as the bases which contain rare-earth ions (L_n) [1.4], CaF_2 - type crystals doped with rare earths proved to be good laser materials

[1.5]. Little attention, however, was paid to intrinsic luminescence of CaF_2 , SrF_2 and BaF_2 crystals. It might be for this reason that only in the early eighties a new type of optical fluorescence was discovered in barium fluoride [1.6, 7], as a result of recombination of holes of the upper core band ($5p$, Ba) with electrons of the valence band ($2p$, F).

Crystals with radiative core-valence (CV) transitions possess the following features:

- 1) short luminescence times (nanoseconds or fractions of nanoseconds, in some samples);
- 2) high thermal stability of all luminescence parameters;
- 3) rather high (about 1 %) radio-luminescence energy yield.

Thus, in non-doped ionic crystals there are two types of radiative transitions, with high efficiencies, namely, excitonic and core-valency ones.

This Chapter is a brief review of experimental and theoretical studies of physical processes due to excitonic and core-valence transitions. The subject matter of the book, namely, search for fast scintillators, has prompted the selection of data for this Chapter.

The study is particularly concerned with ionic crystals that possess effective intrinsic luminescence in the range of room temperatures. That is why the choice of objects under study is confined mainly to fluorides of metals of the second group rather than AHC which have been studied more profoundly. Luminescence features of ionic crystals were studied before in more detail at low temperatures, rather than at room temperature. Application of fast scintillators for high energy physics, however, does not imply cooling of large volumes of crystalline detectors.

1.1. Excitonic Luminescence

1.1.1. Alkaline-Earth Fluorides. First stage of investigation. The processes which are responsible for intrinsic luminescence of alkaline-earth fluorides (AEF) have remained vague as compared to those in AHC. It was shown in [1.8] that a CaF_2 crystal under high-energy excitation produces luminescence in the UV range, and, therefore, can be used as a scintillator. Measurements of Roentgenoluminescence (RL) spectra [1.9, 10] and temperature dependence of light output suggested that luminescence of CaF_2 , SrF_2 and BaF_2 crystals is of an excitonic character. RL spectra of crystals are wide structureless bands with maxima near 300 nm, the shapes of the bands are quite similar to the bands shown in Fig. 1.2, curve 1. A similar UV luminescence band was detected upon cathode excitation [1.11]. The excitonic nature of luminescence of CaF_2 was finally proved during direct optical formation of anionic excitons in the sample (the band $E_{\text{ex}}^{\text{a}} = 11.1$ eV [1.12]). Similar measurements were then made for SrF_2 (11.4 eV by [1.13]). The spectrum of luminescence excitation of

CaF_2 was elaborately measured using synchrotron radiation [1.14]. The distinct structure of the excitation spectrum of intrinsic luminescence of CaF_2 proved to correlate with the reflection band of the crystal [1.15] (as known, AHC exhibit an anticorrelation of reflection spectra with luminescence excitation spectra). An attempt to explain this specific feature of the fluorite involves alternative

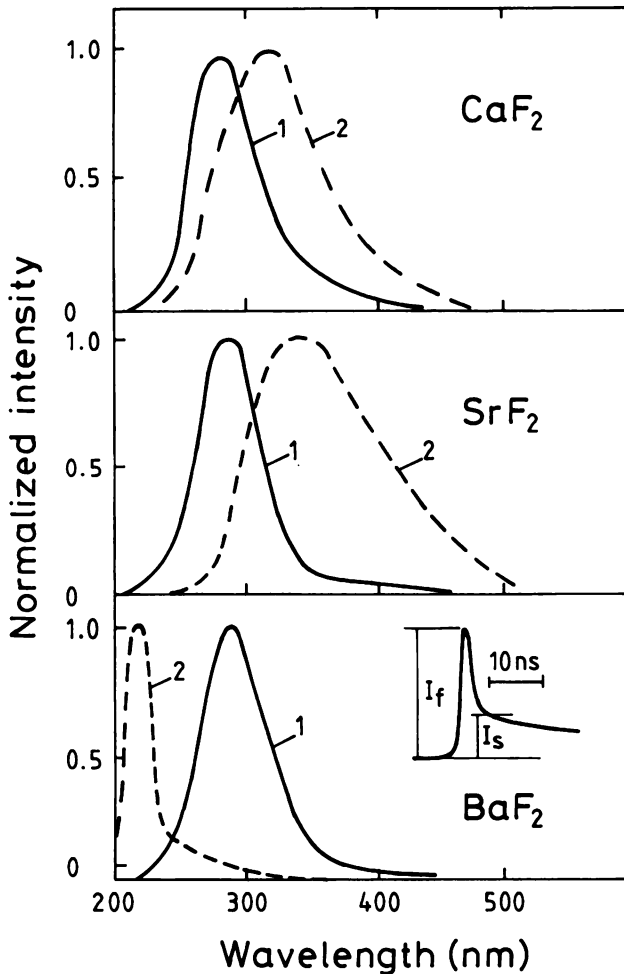


Fig. 1.2. X-ray luminescence spectra of alkaline earth fluorides at 80 K;
 1 - slow component (10^{-6} s) - triplet excitons,
 2 - fast component (10^{-8} s) in CaF_2 and SrF_2 - singlet excitons in BaF_2 (10^{-9} s) - core-valence transitions.
 The insert at the bottom shows the shape of a RL impulse.

channels of transformation of energies of incident quanta: formation of F -centres, photoelectron emission, etc. [1.14].

Bianconi *et al.*, [1.16] report results of measurements of excitation spectra of intrinsic crystal luminescence near the K -edge of Ca absorption (~ 4.05 KeV). The excitation spectrum of RL proved to be antiparallel to the absorption spectrum of the crystal.

Excitonic luminescence of AEF can be detected as well at low energies of incident quanta: $h\nu_1 < E_{ex}^a$. To do that, the sample is first irradiated, then V_k and F -centres are created in it, and, afterwards, electrons are released from the F -centres [1.17] (Fig. 1.1) or from other electronic traps using photoexcitation.

In contrast to AHC, quenching of excitonic luminescence of CaF_2 , SrF_2 [1.10, 13] and BaF_2 [1.10, 18] starts at temperatures that significantly exceed the temperature of V_k centre delocalization. To illustrate this, Fig. 1.3 shows the temperature dependence of light output of the fundamental RL of SrF_2 crystal (Curve 1) [1.19]. A slight low-temperature decrease of light output of SrF_2 with the activation energy $E_a = 26$ meV is not related with V_k -centre delocalization ($T_{del} = 125$ K, $E_a = 0.19$ eV). The temperature quenching of RL of SrF_2 , as well as CaF_2 and BaF_2 starts at 300 K, the activation energy of the process $E_a = 0.33$ eV [1,20]. *Therefore, excitonic luminescence in SrF_2 , CaF_2 and BaF_2 is effective when V_k centres migrate throughout the crystal bulk, too.*

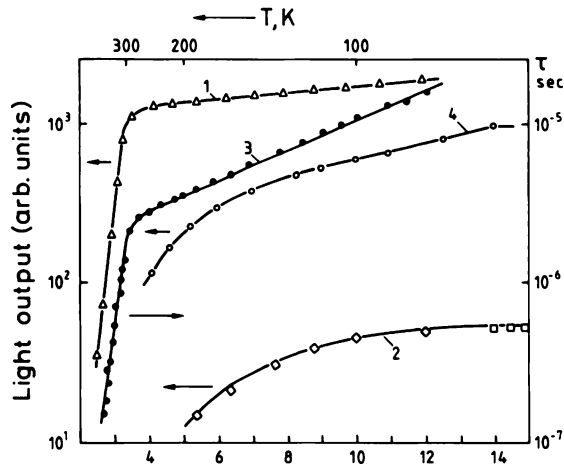


Fig. 1.3. Temperature dependences:

- 1 - light output of the slow component of XRL of SrF_2 ,
- 2 - light output of the fast component of XRL of SrF_2 ,
- 3 - luminescence decay times of XRL of SrF_2 ,
- 4 - light output of XRL of CdF_2 .

Decay time characteristics of intrinsic luminescence. It is known that a V_k -exciton (Fig. 1.1) which, in the case of fluorides is identical to an excited molecular fluorine ion ($F_2^=$)* can be in one of the two excited states: singlet $^1\Sigma_u^+$ and triplet $^3\Sigma_u^+$ [1.2]. In accordance with that, two excitonic luminescence bands are detected in AHC, namely, a σ -band which corresponds to allowed singlet \leftrightarrow singlet transitions and a π -band, which arises from triplet \leftrightarrow singlet transitions. Luminescence of singlet excitons lies within the short-wave spectrum range, has a short decay time (nanoseconds) and is σ -polarized, i.e., the electric field vector E^{\rightarrow} of the emission is parallel to the axis of the V_k centre. The band of triplet excitons has the quantum energies less by about 2 eV than the σ -band, the decay time being about 10^{-6} - 10^{-3} sec, while the vector E^{\rightarrow} is perpendicular to the axis of the V_k centre (π -band) [1.2, 3].

In CaF_2 , SrF_2 and BaF_2 only an intrinsic luminescence band had been detected for a long time, whereas kinetic and polarization data were either not available or scarce, e.g. [1.21]. The authors of [1.10] used for excitation a flash with a pulse duration of 40 ns and came to a conclusion that the constant of intrinsic luminescence decay time of CaF_2 is less than 40 ns. Basing on that, it was established that only singlet excitons are encountered in AEF [1.10, 22]. In fact, CaF_2 , SrF_2 and BaF_2 crystals have a slow (of a microseconds range) component of intrinsic luminescence [1.6, 13]. A fast component in CaF_2 , SrF_2 makes a small contribution to the total light output of crystals only at $T < 200$ K [1.13, 20]. *At a fast excitation the amplitude of the fast luminescence component can be higher than that of the slow one (Fig. 1.2); this is the reason of controversy on conclusions about luminescence decay time of AEF.* Decay time measurements [1.19 - 21] showed that the fast and slow luminescence components of CaF_2 and SrF_2 lie within the same spectrum band. Considerable advances in the understanding of excitonic processes in AEF have been made as a result of experimental research by Williams et al. on measuring time-resolved luminescence spectra and transition absorption [1.23]. It was shown that the crystals have spectrum-overlapping RL components: a fast one $\tau_s = 12$ ns in SrF_2 and 11 ns in CaF_2 and several slow ones, including the most intensive one of the microsecond range. The decay time 12 ns is also given for BaF_2 at 10 K [1.23], however, numerous further experimental studies showed that there is no singlet exciton luminescence in barium fluoride.

Fig. 1.2. shows normalized RL spectra of AEF measured with a selection of a fast (about 10 ns) and slow (1.0 - 50 microseconds) components [1.6]. The band of the fast RL component lies within the long-wave spectrum range (Fig. 1.2). Since this is not in conformity with the behaviour of σ - and π -bands of self-trapped excitons in AEF, it was not quite clear whether the fast

luminescence component in CaF_2 and SrF_2 could be assigned to a singlet exciton or not. Measurements of polarization emission [1.23] did not provide a clear solution either.

It was proved that the long-wave bands in CaF_2 and SrF_2 are assigned to singlet excitons, by way of measuring excitation thresholds of the fast and slow luminescence components within the crystal fundamental absorption region [1.24]. For essentially overlapping bands of the short- and long term RL components this was done using the technique of measuring excitation spectra at a time resolution. Similar to the case of AHC [1.25] in SrF_2 and CaF_2 , smaller quantum energies with respect to the fast σ - RL component (curve 2, Fig. 1.4) correspond to the beginning of excitation of the slow component (curve 1, Fig. 1.4). The position of the excitation threshold of the π - band agrees with the beginning of the crystal fundamental absorption and formation of anion excitons with smaller energies in it (the $\bar{A}_{15} \rightarrow \bar{A}_1$ transitions) [1.26]. The beginning of the formation of singlet excitons in SrF_2 and CaF_2 , apparently, corresponds to the beginning of generation of electron-hole pairs in crystals [1.24].

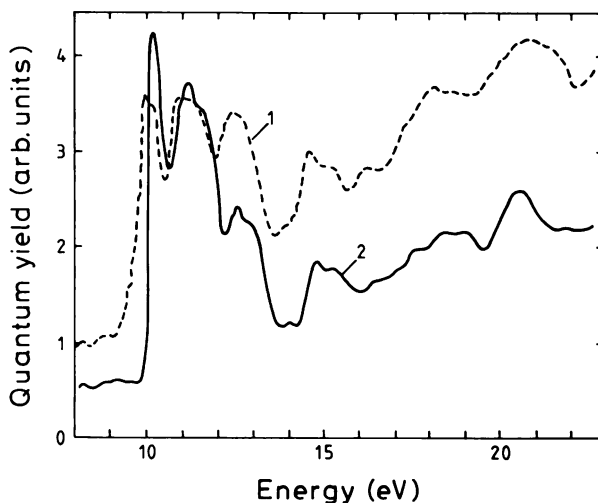


Fig. 1.4. Excitation spectra of (1) slow (microsecond) and (2) fast (about 10 nsec) components of SrF_2 luminescence at 100 K.

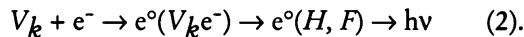
AEF have one more specific feature, namely, the temperature dependences of light output and decay time of triplet excitonic luminescence at $T < 300$ K differ significantly (see Fig. 1.3). To explain this difference, similar to a KCl crystal [1.27], a model of an emitting centre with two closely

located exciton levels is considered. A marked overlapping of spectra of the fast and slow components of RL in CaF_2 and SrF_2 indicates proximity of the singlet and triplet levels of STE in the crystals.

Configuration of the emitting centre - self-trapped exciton. The above characteristics of luminescence of triplet excitons evidence that the configuration of the emitting centre in AEF can differ from that in AHC. These characteristics comprise a high radiation hardness of AEF. Besides, the decay time of the fundamental slow RL component in AEF (dozens of nanoseconds) is less than the typical life times of fluorite triplet excitons: $\tau_t \geq 6 \cdot 10^{-3}$ sec in LiF and NaF [1.28] (for chlorides $1 \cdot 10^{-4}$ sec [1.1]). Therefore, either the symmetry of the emitting centre in AEF is lower against AHC, or the distance between fluorine ions which form an excitonic molecule $(\text{F}_2^-)^*$ in AEF is smaller than that in AHC.

X-ray luminescence detection of paramagnetic resonance showed that the slow luminescence of AEF can be due to the exciton-like state, whose hole component is localized at the centre oriented along the $\langle 111 \rangle$ axis of the crystal [1.29]. These data were later confirmed by EPR experiments upon optical excitation of CaF_2 crystals irradiated in advance [1.30]. Measurements of transitional absorption of STE in AEF (i.e. optical transitions from the excited triplet state of the exciton) led to a model of crystal intrinsic luminescence considered below.

The main specific feature of the structure of crystals with the fluorite lattice is the presence of voids at the centres of cubes formed by fluorine ions. As a result, the molecular ion $(\text{F}_2^-)^*$ whose axis is directed along $\langle 100 \rangle$, upon the entrapment of an electron can turn its axis towards the $\langle 111 \rangle$ direction of the crystal, i.e., to a position typical of an *H*-centre in AEF [1.31]. A slight shift of the molecule $(\text{F}_2^-)^*$ along its axis will make one of the ions of the $(\text{F}_2^-)^*$ molecule occupy a nodal site, and the other one will occupy the centre of the fluoride cube. The stages of these processes are shown in Fig. 1.5. As a result of the rotation of the axis of the $(\text{F}_2^-)^*$ molecule, a state which is similar to the nearest *F*- and *H*-centres, i.e., similar to the *F* - *H* pair (Fig. 1.5 d), is formed. Consequently, the following reaction corresponds to intrinsic luminescence in AEF:



The STE transition $\langle 100 \rangle \rightarrow \langle 111 \rangle$ is accompanied by lowering the symmetry of the luminescence centre from D_{2h} to C_{1h} . In this case the fluorine ions contained in the low-symmetry (C_{1h}) STE are in nonequivalent positions. The first one is at the nodal site, the second one is at the interstitial site, Fig. 1.5. This results in respectively short (microsecond) life times of triplet excitons in AEF.

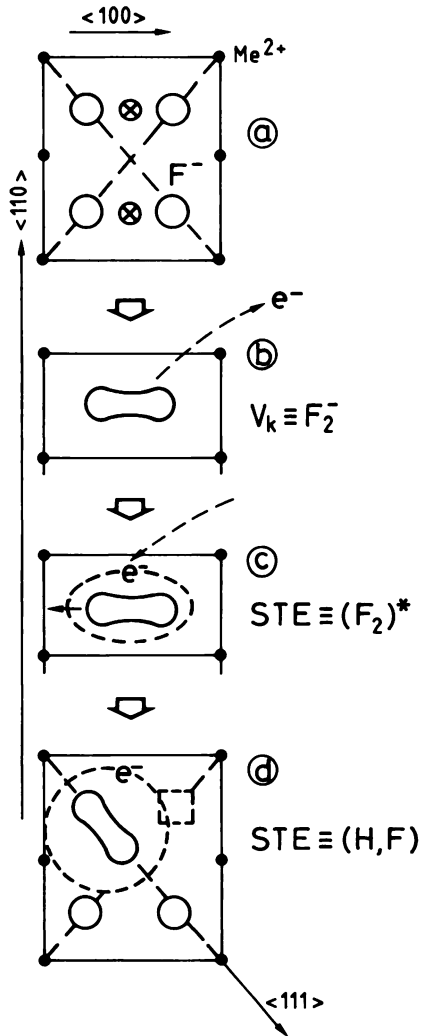


Fig. 1.5. Models and stages of development of a self-trapped exciton (STE) in MeF₂ crystals with the fluorite lattice:

- initial location of ions in the (111) plane of the crystal (Me²⁺ ions beyond the plane are denoted by a cross);
- V_k-centre or a F₂ molecular ion;
- a self-trapped exciton as a V_k-centre which has entrapped an electron or a F₂ molecular ion;
- a self-trapped exciton as a H-centre and a F⁻ centre.

It was shown later that in some AHC a self-trapped exciton is a centre having C_{2v} symmetry and is practically identical to a $F - H$ pair [1.32]. Thus, alkaline-earth fluorides have played the role of model objects for alkali halide crystals [1.32, 33].

It is worthwhile mentioning that investigation of excitonic processes in AEF is far from being completed. There are still many vague features of the mechanism of intrinsic luminescence, namely:

- what is the configuration of singlet excitons? In EPR experiments [1.29] only a slow RL component was detected. The temperature dependence of the intensity of the fast RL component of CaF_2 and SrF_2 (Fig. 1.3, curve 3) and polarization characteristics of radiation [1.23] indicate a possible σ -emission at the stage of a $V_k e^-$ exciton:
- is the high thermal stability of light output of the crystals related to (H, F) configuration of the radiative centre? The point is that the model of a $F - H$ exciton is considered as well for a CdF_2 crystal with the fluorite-type lattice that does not possess thermal stability of luminescence (curve 4, Fig. 1.3);
- does the rotation $\langle 100 \rangle \rightarrow \langle 111 \rangle$ occur at the moment when an exciton is generated or does the state $e^\circ(V_k e^-)$ migrate throughout the crystal and is transformed into the state $e^\circ(H, F)$ only near an impurity or a defect?

1.1.2. Other Fluorides. The situation is quite peculiar as it is difficult to find such crystals, besides AEF, in which excitonic luminescence has a high efficiency at room temperature. Excitons are simply unstable at high temperatures. CsF , RbF and KF crystals (the latter to a smaller extent) undergo core-valency transitions (see below). An effective fast scintillator CsI has RL, evidently, of a non-excitonic origin [1.34]. In LaF_3 , CeF_3 and other crystals there are no excitonic peaks in the absorption spectra and, moreover, no excitonic luminescence. Cerium fluoride is a self-activated crystal, i.e. the luminescence is due to $d - f$ transitions of a Ce^{3+} ion. In MgF_2 , LiF , NaF , KMgF_3 , KCaF_3 crystals, etc., excitonic luminescence is practically quenched at room temperature.

In a CdF_2 crystal which is very similar to AEF crystals in its properties a 370 nm luminescence band of an excitonic origin is known [1.35]. The intensity of RL upon temperature rise in the range 77 - 300 K is quenched with the activation energy $E_a \sim 75$ meV (curve 4, Fig. 1.3) At room temperature the RL energy output of CdF_2 is 0.03%, the decay time is 7 ns. These parameters allow one to consider CdF_2 as a promising scintillator [1.36]. In ZnF_2 RL with the decay time 20 ns and energy yield 0.1 % was detected.

For some applications (e.g., in high energy physics) the most important parameters are a high density of the crystal (the efficiency of gamma quanta absorption) and a short luminescence decay time.

Although the requirements for RL yield are not too strict, it is essential to know whether the RL level upon excitation by relativistic particles exceeds that of Cherenkov radiation or is lower. Some advantages of Cherenkov radiators are reported in Chapter 3.4. This can be illustrated by the crystals HfF_4 with the density 7.13 g/cm^3 with $\tau = 29 \text{ nsec}$, ThF_4 (7.56 g/cm^3 , 25 nsec); BaYb_2F_8 (7.01 g/cm^3 , 1.5 nsec); PbF_2 (7.76 g/cm^3), YbF_3 (8.17 g/cm^3), CsPbF_3 , $\text{Pb}(\text{Zn,Th})\text{F}_6$, in which the RL intensity is mostly low [1.37].

1.2. Core-Valence Transitions

1.2.1. Physical Mechanism. The advances in knowledge about core-valence transitions are considered in papers [1.38, 39]. The authors of [1.6] had failed to relate the luminescence band at 220 nm (Fig. 1.2) with the decay time 0.8 ns in BaF_2 with excitonic luminescence, and it had been attributed to a CV transition [1.7]. It was shown later that this fast luminescence component of BaF_2 extends up to the VUV spectrum range [1.40]. Curve 1 in Fig. 1.6 shows the spectrum of subnanosecond luminescence component of BaF_2 , with two maxima, 5.6 eV and 6.4 eV.

Let us consider the physical processes which are responsible for CV transitions. Fig. 1.6 shows schematically the energy bands of a BaF_2 crystal, constructed on the basis of optical [1.14,15] and photoemission data [1.41], confirmed by calculations [1.42]. Usually luminescence transitions (excitonic, impurity ones) occur within the upper gap of the crystal, E_{g1} wide. Under a high energy excitation, holes are formed in the valence band ($2p$, F^-) as well as in the upper core band ($5p$, Ba) of the crystal. After "floating" up to the top of the core band the hole can recombine with the electron of the valence band. Hole transitions between the upper core band and valence bands of the crystal were called core-valence transitions [1.63]. Fig. 1.6 shows appropriate electron transitions. These transitions occur in the region of the second energy gap of the crystal E_{g2} or the gap between the core and valence bands. In recent times the luminescence due to the transitions considered here has been called core-valence luminescence [1.43].

There are other names which, in our opinion, are less suitable, eg., Auger-free luminescence [1.34], cross-luminescence [1.37]. We stick to the term 'core-valence transitions' because it describes the essence of the physical process which is responsible for the detected luminescence. The term 'Auger-free luminescence' specifies the condition of an insufficient transition energy for excitation of Auger electrons from the valence band of the crystal ($h\nu_r < E_{g1}$). In this case radiation reabsorption is not taken into account. Most radiation emitted in the energy band $E_{\text{ex}}^a < h\nu_r < E_{g1}$ can be just reabsorbed

by the crystal and anionic excitons will be formed, i.e., luminescence will be quenched without formation of Auger electrons.

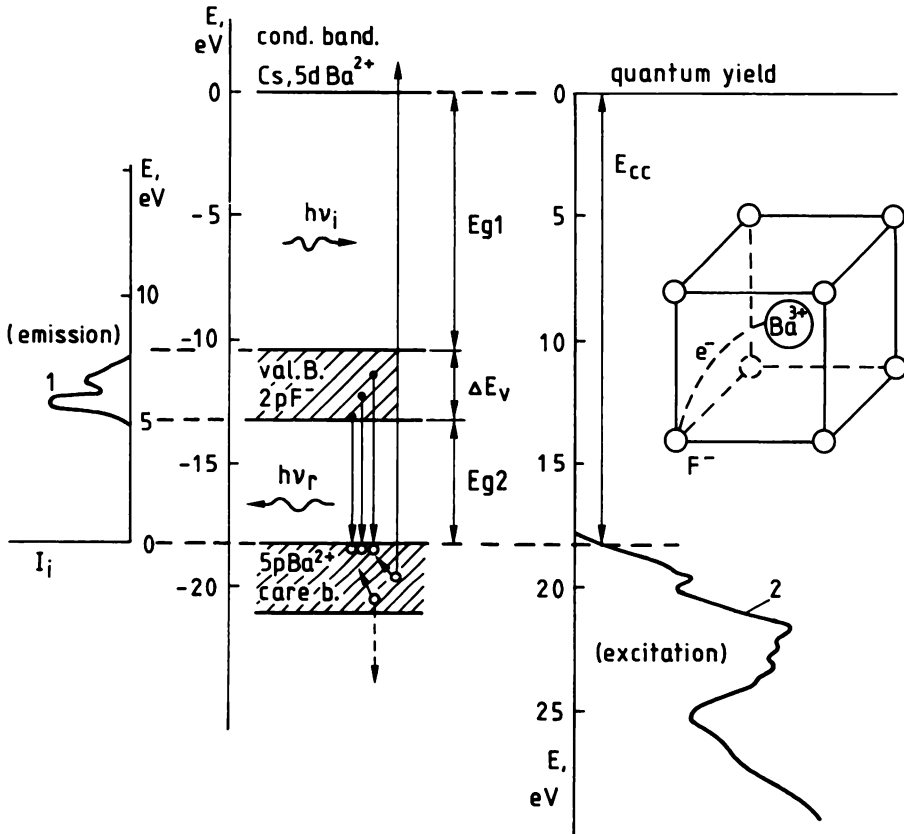


Fig. 1.6. Scheme of energy band of a BaF₂ crystal and possible electronic transitions:

- 1 - core-valence luminescence spectrum;
- 2 - spectrum of luminescence excitation in the crystal

A fragment of BaF₂ structure and the electronic transition which corresponds to CV transitions is shown on the right

The term 'cross-luminescence' is not quite suitable either, because, first, it implies cross-transitions, i.e., transitions that involve more than one ion, namely, cations and anions (in the general case - ions of different elements). In this respect common luminescence also could be called cross-luminescence, because it involves electrons of the conductivity band formed mostly by cations, and the holes of the valence band, formed by anionic states. Second, usually the first part of the terms which refer to various kinds of

luminescence indicate the kind of excitation (cathode, photo, electro, etc.). Finally, 'cross-luminescence' reminds one of cross-relaxation which denotes a phenomenon of a totally different physical sense.

Another approach used for consideration of CV-transitions is a cluster one. As a result of relaxation of the core hole, a Ba^{3+} ion surrounded by F ions is formed (Insert, Fig. 1.6.). The transition with the charge transfer from an F^- ion to a Ba^{3+} ion corresponds to a core-valence transition in the $[BaF_8]$ cluster.

The following facts, which were obtained experimentally, prove that the detected luminescence of a crystal is attributed to CV transitions:

1. In the luminescence excitation spectrum (curve 2, Fig. 1.6) a threshold is detected, at which the energy of incident quanta ($h\nu_i$) exceeds the energy gap E_{CC} between the upper core band and the conduction band. The condition $h\nu_i > E_{CC}$ has been checked for about 20 compounds now. Hence, radiative CV transitions occur only provided that holes are formed in the upper core band. It was shown in [1.7, 38] that the core (cationic) excitons cannot be responsible for the detected luminescence;

2. As the transitions occur between the top of the core band and various levels of the valence band (Fig. 1.6) [1.38], the low energy edge bands of the CV luminescence correspond to the width of the second energy gap E_{g2} , while the width of luminescence band is defined by the width of the valence band of the crystal (ΔE_v), i.e., the following condition exists:

$$E_{g2} \leq h\nu_r < (E_{g2} + \Delta E_v) \quad (3),$$

where $h\nu_r$ is the quantum energy of CVT.

The condition (3) was checked reliably for about 15 crystals. It is evident from Fig. 1.6 (curve 1) that the spectrum of the subnanosecond component of luminescence in BaF_2 meets the condition (3);

3. The decay time of CV luminescence is within the range from 0.6 to ~ 3 ns in various crystals. The recently made calculations of the probability (rate) of transitions of the type ($5p, Ba$) \rightarrow ($2p, F$) [1.44] and ($5p, Cs$) \rightarrow ($3p, Cl$) [1.45] are in a good agreement with the experiment;

4. Parameters of CV luminescence do not strongly depend on temperature within a wide temperature range. For instance, RL yield and decay time in BaF_2 remain almost unchanged within the range 77 - 850 K [1.46]. Upon temperature rise the values of E_{g1} and ΔE_v decrease, while the gap E_{CC} is but slightly changed, therefore, the bands of CV luminescence should be shifted to the short-wave range. A slight shift of the bands was detected experimentally. The transition time should decrease with temperature fall due to a shorter distance between ions and a larger overlapping of wave functions of appropriate ions ($2p, F$ - $5p, Ba$). A slight

temperature change of the decay time was detected, for instance, in BaF₂: at 150 -370 K $\tau = 0.89 \pm 0,05$ ns, while at T = 10 K it was equal to 0.81 ns [1.47].

1.2.2. Conditions of Detection. To avoid radiation reabsorption and the Auger effect, the condition $h\nu_r < E_{ex}^a$ should be fulfilled, i.e., quanta energy of CV luminescence should be less than that of the formation of anionic excitons in the crystal. Besides, detection of CV-luminescence requires a gap between the core and valence bands, $E_{g2} > 0$. Taking into account that $E_{g1} \sim d^{-2}$ and $\Delta E_v \sim d^{-2}$ [1.48] where d is the distance between the close ions in the crystal, the author of [1.38] obtained the following condition for detection of CV-luminescence without losses:

$$1.34 < (E_{ex}^c/E_{ex}^a = \gamma) < 2 \quad (4),$$

Table 1.1

Parameters $E_{ex}^c/E_{ex}^a = \gamma$, i.e., ratio of the energy of formation of low-energy core excitons to the energy of formation of anionic excitons in AHC

| anion cation | F | CL | Br | I |
|-----------------|----------------------------|-----------------------------|-----------------------------|----------------------------|
| NA | $\frac{33.1}{10.5} = 3.15$ | $\frac{33.3}{7.738} = 4.30$ | $\frac{33.1}{6.478} = 5.10$ | $\frac{32.9}{5.39} = 6.10$ |
| K | $\frac{19.7}{9.72} = 2.03$ | $\frac{20.1}{7.70} = 2.61$ | $\frac{19.8}{6.57} = 3.01$ | $\frac{20.1}{5.83} = 3.57$ |
| Rb | $\frac{16.1}{9.31} = 1.73$ | $\frac{16.2}{7.48} = 2.17$ | $\frac{16.2}{6.47} = 2.50$ | $\frac{16.3}{5.55} = 2.94$ |
| Cs | $\frac{13.0}{9.13} = 1.42$ | $\frac{13.2}{7.62} = 1.73$ | $\frac{13.1}{6.63} = 1.98$ | $\frac{13.1}{5.62} = 2.33$ |

i.e., the relation between the energy of formation of the core (cationic) exciton E_{ex}^c and the energy of formation of the anionic exciton E_{ex}^a should be within certain limits. Table I.1 presents these values as well as the

parameter γ for AHC which have been studied most profoundly [1.49]. The correctness of the condition (4) is confirmed experimentally. In crystals of RbF [1.50, 51], CsF and CsCl [1.51, 52] the authors detected luminescence which corresponded to CV luminescence in all the parameters, the less was the parameter γ , the less was the energy of quanta radiation. In CsBr CV-transitions are effective only at 77 K, while upon sample heating up to room temperature the light output of radiative luminescence decreases by a factor of about 100 [1.50, 52].

In a KF crystal a low-energy part of the band of CV-luminescence was detected, while the high-energy part was reabsorbed by the sample [1.53]. In RbCl weak luminescence was detected at a low temperature, which, apparently, was a part of the band of CV-luminescence [1.56]. In other AHC, as seen from Table I.1, detection of CV luminescence is impossible.

In alkaline-earth fluorides, for BaF₂ $\gamma = 1.75$, SrF₂ $\gamma = 2.16$ and CaF₂ $\gamma = 2.49$. It is essential that the condition [1.4] can be fulfilled in alkali halides, whereas for oxides it cannot be fulfilled, in fact. For other compounds it can hardly be fulfilled as well [1.38].

For many crystals the values E_{ex}^a and E_{ex}^c have not been measured (especially, the latter). As the bonding energy of core and anionic excitons is not large (~ 1 eV), we can assume that $\gamma = E_{ex}^c/E_{ex}^a \approx E_{cc}/E_{g1}$. The value E_{cc} can be regarded as the depth of the upper core band (Fig. 1.6).

As seen from the data presented in Table I.1, the value of E_{ex}^c (and, consequently, E_{cc}) is defined by the type of cation and is hardly dependent on the type of anion. The depth of the upper core band in any halide proved to be close to the bond energy E_b of the electron of the outer populated shell of the appropriate free atom [1.38]. Then the condition (4) for some metal halides can be transformed to:

$$12 \text{ eV} < E_b < 19 \text{ eV} \quad (5)$$

Therefore, if one knows the bonding energy of electrons in the atom, one can find whether that atom can be used as a cation in the crystal with CV luminescence. Table I.2 lists E_b values for the atoms which form ions with a populated outermost shell. The ions with an underpopulated outermost shell (ions of the iron group, lanthanides, etc.) are not considered, because their presence in the crystal impairs the fulfillment of the condition (4). In Table I.2 the elements are divided into four groups according to the conditions of detection of CV-luminescence in alkali halides of the appropriate cations. The elements in column 1 have low bond energies of electrons E_b , that is why the non-overlapping of the upper core and valence bands is possible only in appropriate iodides and bromides (the valence band of the crystal is "raised" as well upon replacement of a halogen in the series of F, Cl, Br, I).

Table 1.2
Energies (eV) of electron bonds against the vacuum level in free atoms which create ions with a populated outermost shell

| outermost shell of ion | 1 | 2 | 3 | 4 |
|------------------------------|---|---|------------------------|--|
| | $\gamma \lesssim 1.34$ | $1.34 \leq \gamma \leq 2$ | $\gamma \gtrsim 2$ | $\gamma > 2$ |
| $2p^6$ | | | | Na ⁺ , .34 |
| $3p^6$ | | | *K ⁺ , .19 | Sc ³⁺ , .33 Ca ²⁺ , .28 |
| $4p^6$ | | *Rb ⁺ , .16 | Sr ²⁺ , .23 | Zr ⁴⁺ , .35 Y ³⁺ , .30 |
| $5p^6$ | | Cs ⁺ , .14 Ba ²⁺ , .18 | La ³⁺ , .22 | Ce ⁴⁺ , .25 |
| $6p^6$ | | *Fr ⁺ , .18 | | *Th ⁴⁺ , .33 *Ra ²⁺ , .25 |
| $3d^{10}$ | Cu ⁺ , .11 | Zn ²⁺ , .12 | Ga ³⁺ , .21 | Ge ⁴⁺ , .33 |
| $4d^{10}$ | Ag ⁺ , .11 | Cd ²⁺ , .14 | In ³⁺ , .21 | Sn ⁴⁺ , .29 |
| $5d^{10}$ | | Au ⁺ , .12, .5 Hg ²⁺ , .14 | Tl ³⁺ , .21 | Pb ⁴⁺ , .27 |
| $5s^2$ | In ⁺ , .10 Sn ²⁺ , .12 | Sb ³⁺ , .15 | | |
| $6s^2$ | Pb ²⁺ , .10 Tl ⁺ , .10, .4 | Bi ³⁺ , .12 | | |

Note: elements that have radioactive isotopes are denoted by an asterisk

The condition of detection of CV-luminescence is met for elements of column 2. Yet, CV luminescence has been found only in alkali halides of Rb, Cs, Ba. Luminescence is efficient only between the p -shell of cation and p -shell of anion, i.e., ($p \rightarrow p$) transitions, forbidden for a particular ion or atom, are detected. Core-valence ($p \rightarrow p$) transitions become possible due to contributions of states of various types (s , d) of cations to molecular orbitals of the valence band [1.45].

CV-luminescence was not found in cadmium halides [1.54]. For other ions of column 2 with the outer d -shell (Zn^{2+} , Hg^{2+}) or s -shell (Sb^{3+} , Bi^{3+}) no data on detection of CV-luminescence are available. Apparently, in the CdF_2 , $CdCl_2$, $CdBr_2$ crystals (for which the condition (4) is fulfilled) ($s - p$)-hybridization prevails, that gives rise to levels in the valence band. Transitions from those levels to the core band are forbidden. Theoretical investigations are required to explain the absence of ($d \rightarrow p$) and ($s \rightarrow p$) CV-transitions.

Fluorides of the ions presented in column 3 of Table I.2 nearly fulfill the conditions of detection of CV-luminescence. In multicomponent fluorides (eg., $KMgF_3$) which contain an additional cation (or cations) with high ionization energies, the range of limiting values of E_B in the inequality (5) rises up to 20 - 22 eV. We see from the data presented in Table I.2 that potassium is an active ion for CV-transitions in multicomponent fluorides. In $KMgF_3$ and $KCaF_3$ crystals the condition (4) is fulfilled and CV-luminescence is detected without losses at room temperature [1.56].

The ions from column 4, Table I.2, cannot participate in CV-transitions, they can be used only as additional ions in multicomponent alkali halides.

Thus, there is a limited number of ions, namely, K^+ , Rb^+ , Cs^+ and Ba^{2+} which are active with regard to CV-transitions. Nevertheless, possibilities of search for compounds possessing CV luminescence are wide enough.

1.2.3. Experimental Results. Table I.3 presents the main parameters of luminescence of crystals in which CV-transitions are responsible for luminescence. Spectrum and decay time parameters of luminescence were measured both at high-energy ($h\nu_1 \gg E_{cc}$) excitations [1.53 - 60] and at UV (synchrotron) excitation in the range $h\nu_1 \cong E_{cc}$ [1.61 - 68]. As a rule, these parameters are close for both types of excitation. The energy yield of luminescence (relation of the energy of a luminescence light to that of incident gamma or X-ray quantum) was determined indirectly, that is why its values are, in fact, estimations. Let us consider specific features of luminescence of crystals for four p -cations, which are involved in CV-transitions.

Table 1.3.
Parameters of core-valence luminescence in uni- and bicationic
halides at room temperature

| CRYSTAL | maxima of emission bands (eV) | emission range (eV) | excitation threshold (eV) | decay time (nsec) | energy yield (%) | refer- ences |
|---------------------------------|--|---------------------------|---------------------------------|-------------------------|------------------------|------------------|
| BaF ₂ | 5.6; 6.4 | 5.2-7.3 | 18.23 | 0.8 [±] 0.1 | 0.6 | [52] [7][47] |
| BaLiF ₃ | 5.8; 6.7 | 5.0-7.6 | 18 | ≈1.0 | 0.4 | [59] |
| BaMgF ₄ | 5.6; 6.5 | - | 18 | - | 0.3 | [59] |
| BaY ₂ F ₈ | - | - | 19.3 | ~3 | ~0.2 | [61] |
| CaF | 3.2 | 2.5-4.2 | 14.1 [±] 0.2 | 2.9 | 0.8 | [51][52] |
| CaCl | 4.4; 5.2 | 4.0-5.85 | 14.1 | 0.88 | ~0.2 | [51][52] |
| CaMgCl ₃ | 4.4; 5.1 | 2.6-5.6 | 14.1 | 2.1 | - | [58][62] |
| CaCaCl ₃ | 4.0; 4.9 | 3.1-5.5 | 14.0 | 1.7 | ≥1.0 | [63] |
| CaSrCl ₃ | 4.1; 4.9 | 3.2-5.4 | 13.5 | 2.0 | ~1.0 | [62][68] |
| CaBr | 5.0; 6.0 | 4.5-6.66 | 13.82 | 0.07 | 0.008 | [50][52] |
| CaCaBr ₃ | 4.4; 5.4 | 3.2-6.0 | 14.0 | 0.8 | - | [64] |
| CaSrBr ₃ | 4.4; ~5.0 | 3.1-6.0 | 14.0 | 0.8 | - | [64] |
| RbF | 5.2 | 4.7-6.2 | 16.8 | 1.3 | 0.7 | [50][51] |
| RbMgF ₃ | 4.2 | 2.8-6.2 | - | 2.1 | 0.1 | [55][65] |
| RbCaF ₃ | 4.3 | 3.0-5.8 | 16.8 | 2.82 [±] 0.04 | ≥1.0 | [60][65] |
| RbY ₂ F ₇ | - | - | 17.5 | - | - | [66] |
| KMgF ₃ | 7.2; 8.0 | 5.3-9.1 | 22.0 | 1.5 [±] 0.3 | ~0.6 | [56] [53][55] |
| KCaF ₃ | 7.3; 8.0 | 6.0-8.9 | - | ≈ 2 | ~0.6 | [55][56] |
| KYF ₄ | 7.3 | - | 21.0 | 1.9 [±] 0.4 | 0.3 | [67] |
| K ₂ YF ₅ | 7.6 | 5.5-8.5 | - | 1.3 [±] 0.3 | 0.1 | [55][57] |
| KLuF ₄ | 7.6; 6.7 | 5.5-8.9 | 20.8 | 1.3 [±] 0.3 | 0.05 | [57][67] |
| KLu ₂ F ₇ | 7.5 | - | 21.0 | ≈ 2 | 0.03 | [57] |

The barium group. As seen from the data presented in Table I.3, barium fluoride exhibits the maximum light output among Ba-based crystals. The light output is reduced when the crystal contains some rare-earth ions R^{3+} (except La and Ce), as impurities [1.69] or as the ions (Tm, Yb, etc.), which are contained in the chemical formula, e.g. BaR_2F_8 [1.61]. The main ($4f$) and excited ($5d$) level of the R^{3+} ion enters the forbidden zone of BaF_2 , thus reducing the transmission of the crystal in the short-wave spectrum range and impairs the fulfillment of the condition (4).

In some cases $Ba_{1-x}R_xF_{2+x}$ crystals with low R^{3+} contents ($< 0.1\%$) exhibited a marked decrease in the intensity of the 300 nm band upon a slight decrease in the intensity of the 220 nm band [1.69] (the slow component is often unwanted). For instance, in the crystals of $BaF_2:Dy$ (0.01 mole %) the slow RL component is almost missing, and in $BaF_2:La$ (0.2 mole %) and $BaF_2:Ce$ (0.2 mole %) [1.70] a slight increase in intensity of the 220 nm band, as compared to a pure BaF_2 crystal, was found.

In $BaLiF_3$ the yield of the slow (excitonic) components of radiative luminescence is also less than that in BaF_2 [1.59]. One more positive feature is that the density of $BaLiF_3$ (5.23 g/cm^3) is higher than that of BaF_2 (4.88 g/cm^3).

In $BaCl_2$ crystal CV-luminescence bands should lie within the range 6 to 8 eV, however, such luminescence has not been detected experimentally [1.71]. The detected luminescence of $BaBr_2$ at 420 nm [1.71] can hardly be regarded as a CV-transition. Probably, luminescence of BaI_2 (220 nm, 6 nsec) [1.71] is part of the band of CV-transitions.

The cesium group. Due to low ionization energies (14 eV) of $5p$ electrons the condition (4) is fully met only in one fluoride - CsF crystal. The properties of cesium fluoride are well known as it is used as a fast scintillator [1.72]. According to estimations, $CsSrF_3$ crystal is close to the requirements of condition 4.

$CsCaCl_3$ and $CsSrCl_3$ have good scintillation parameters (Table I.3). The slow component of RL is insignificant in those crystals. On passing over from $CsBr$ to $CsCaBr_3$ and $CsSrBr_3$, scintillation parameters become better [1.64].

At 77 K the light output of bicationic bromides is larger by a factor of about 10 than in $CsBr$, the decay time is 2.3 nsec in $CsCaBr_3$ and 2.6 nsec in $CsSrBr_3$. For these compounds, as it follows from the excitation spectra of luminescence, a substantial contribution of excitonic luminescence (especially at low temperatures) to the total light output is typical. •

The rubidium group is represented by several fluorides (Table I.3). In principle, the condition of detection of CV-luminescence is met in the

RbCaCl₃ crystal, in which RL in the UV range was detected [1.43]. RbCaF₃ is one of the best scintillators; it was used for studying the influence of the structural phase transition on luminescence parameters of the compound [1.65].

The potassium group is represented by fluorides only (Table I.3); in other potassium alkali halides the condition 4 cannot be fulfilled. In a KF crystal the condition of detection of CV transitions was partially fulfilled, i.e.,

$$E_{g2} < E_{ex}^a < (E_{g2} + \Delta E_v) \quad (6)$$

That is why only the low energy part of the band of CV-luminescence was detected in KF at 77 K. Upon temperature rise the crystal fundamental absorption edge is shifted to the long-wave part and at room temperature the CV luminescence in KF is, in fact, fully reabsorbed by the crystals (a similar case is observed in a CsBr crystal).

The presence of a cation (Mg²⁺, Ca²⁺, Y³⁺) with a high ionization energy of outer electrons (column 4 in Table I.2) in the crystal results in a wider forbidden band E_{g1}, i.e., better conditions for emission of quanta of CV luminescence from the crystal. In KMgF₃, KCaF₃ and KYF₄ crystals the condition 4 is met also at room temperature and these crystals possess an intensive fast CV luminescence.

Studies of thermal stability of luminescence output in crystals are scarce. As is known, RL yield is changed insignificantly in BaF₂ and CsCl up to 850 K [1.46], in CsF and RbF - up to 600 K [1.51]. The following temperatures correspond to the thermal quenching of luminescence: 700 K in BaF₂, LaF₃ 540 K in KMgF₃ [1.53]. *The high thermal stability of luminescence evidences a local character of the process and a weak interaction of the core hole with phonons. This confirms the cluster model of CV luminescence as well.*

We shall now dwell upon common features of simple AX crystals and ABX₃ crystals with the perovskite structure, where A is an ion of a univalent metal, B is the ion of a divalent metal, X is a halide ion. On passing over from AX to an appropriate ABX₃ compound, the luminescence decay time increases and the light output is also increased (Table I.3). The increase of the decay time can be attributed to a larger r(A - X) distance between the closest ions A⁺ and X⁻, which are involved in CV transitions. The r(A - X) distances in crystals are as follows: CsCl - 3.67 Å, CsCaCl₃ - 3.81 Å, RbF - 2.82 Å, RbCaF₃ - 3.14 Å, KF - 2.67 Å, KMgF₃ - 2.8 Å. As r increases, the overlapping of wave functions of and X⁻ ions becomes smaller and, accordingly, the probability of radiative CVT is smaller.

It is more difficult to explain a larger energy yield of luminescence η upon the transition $AX - ABX_3$. The point is that this increase is observed only under X -ray or gamma excitation ($h\nu_i \gg E_{cc}$), while at optical excitation ($h\nu_i \cong E_{cc}$) the ratio of luminescence yields of crystals can be different. For instance, at VUV excitation (21.4 eV) the yield of the fast luminescence component in CsF is smaller by a factor of 10 than that in BaF₂ [1.71], while under X -ray excitation CsF exhibits a larger yield, than BaF₂ (Table I.3). At a high-energy excitation the luminescence yield is determined first of all by the amount of holes in the core band relative to the total number of holes [1.38].

If the probability of the transition $A^+ \rightarrow X^-$ is approximately the same in the pair of crystals of AX, ABX_3 , then, the more holes in the upper core band of the crystal, the higher CV luminescence output. If, however, most holes are located in the valence band, the excitonic luminescence output is higher. It is clear from this model that when a ABX_3 crystal contains a B^{2+} cation whose appropriate core band is located slightly lower than the npA^+ band (see Fig. 1.8) there are better conditions for holes of deep levels (bands) to appear in the upper core band. In the competitive processes of formation of valence and core holes the latter prevails and the yield (number) of CV transitions increases.

Thus, while considering the hole relaxation process one should take into account the model of crystal energy bands, although the cluster model with an account of band considerations is preferable for the description of the final luminescence act.

Changing the type of cation B in ABX_3 crystals and other multicomponent compounds one can control decay time characteristics of luminescence by monitoring the participation of excitonic and core-valence transitions. There is one more type of transitions which yields fast scintillation, namely, interconfiguration $d \rightarrow f$ transitions in rare earth ions [1.69].

Table I.3 does not comprise all the compounds in which radiative CV-transitions are possible, that is why of interest are CsSrF₃, CsScF₄, RbAlF₄, Ba₃Al₂F₁₂, KY₃F₁₀, etc. crystals.

The example of the pair CsBr, CsSrBr₃ indicates that the *crystal structure of an object is not fully responsible for the efficiency of radiative CV transitions*. Apparently, at the final stage the anion - cation charge transfer process occurs between two closely located ions, i.e., the cluster model is effective (insert, Fig. 1.6). In this case the appropriate transitions can be expected, such as ($5p, Ba^{3+}$) \rightarrow ($2p, F^-$); ($5p, Cs^{2+}$) \rightarrow ($3p, Cl^-$), etc., in solid solutions, glasses and ceramics.

1.2.4. Theory. Core-valence transitions have been insufficiently studied in terms of theory. Using the formerly obtained exact single electron Hartree-Fock wave functions for barium and fluorine, in paper [1.44] we calculated the matrix element of a dipole moment of the transition ($5p, \text{Ba}^{3+}$) \rightarrow ($2p, \text{F}^-$). The probability of this transition in BaF_2 is 0.7 nsec, which is close to the experimental value of the constant of crystal luminescence decay.

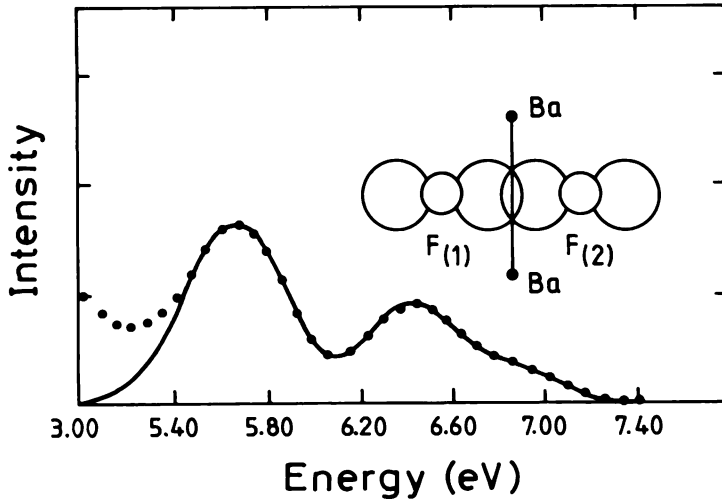


Fig. 1.7. Luminescence spectrum of BaF_2 at room temperature: experimental data are denoted by dots, solid curve denotes simulations for CVT. Top right: a cluster which defines the width of the valence-band in the crystal

In [1.45, 73] a self-consistent cluster technique of scattered waves was applied and a single electron approach was used for calculation of the shape and parameters of CsCl and CsBr luminescence spectra. The core hole, which is involved in the CV transition is regarded as quasimolecular multicomponent $[\text{CsCl}_8]$ and $[\text{CsBr}_8]$, accordingly. The calculated energies of the maxima in luminescence spectra of CsCl and CsBr are in a good agreement with the experimental data. The obtained transition times agree with the experimental data as well [1.73].

Dutch physicists are developing an interesting and informative approach [1.74]. For a BaF_2 crystal, molecular orbitals in the form of linear combinations of atomic orbitals (LCAO) have been calculated using the Hartree-Fock technique. The rate of transitions from the excited $(\text{Ba}^{3+}\text{F}_8)^{5-}$ and core $(\text{Ba}^{2+}\text{F}_8)^{6-}$ cluster states was determined.

Fig. 1.7 shows a RL spectrum of BaF_2 against the calculated spectrum [1.74]. A good agreement between theoretical and experimental data both in

spectral composition and radiation intensity was obtained, as well as in the probability of CV transitions in BaF_2 . The two main maxima of luminescence, 5.6 eV and 6.4 eV, are attributed to bonding and antibonding $2p$ orbitals of fluorine, accordingly. Similar calculations, made recently [1.55] for crystals with the perovskite-type structure, BaLiF_3 and KMgF_3 , show a worse agreement with the experiment.

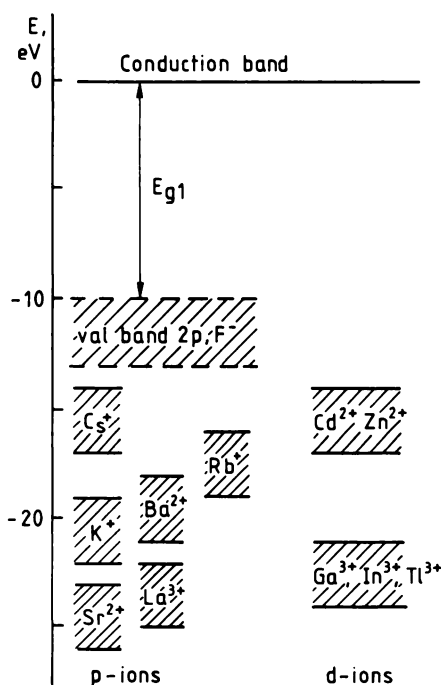


Fig. 1.8. A simplified scheme of energy bands of fluorides which are promising for search for CV luminescence

Both theoretical and experimental data show that it is difficult to obtain scintillation decay times much shorter than 1 nsec using CV transitions. The decay time values of the order of 10^{-10} sec can be obtained using direct CV transitions (within the limits of an ion) [1.38] or transitions between core bands [1.44].

1.2.5 Prospects for Research. It is clear from the data presented in Table I.3, that the energy yield η of scintillators based on CV transitions, at

most, slightly exceeds 1 %. The problem of increase of η and control of spectrum composition can be solved by incorporation of the ions which are active with regard to CV transitions to various matrices, crystalline or amorphous, possessing a low (or zero) yield of CV luminescence. The two types of crystals which are similar in properties, are promising: crystals that possess impurity CV transitions and crystals with overlapped core bands. It is clear from the generalized scheme of energy bands that the CV active ions are Cs^+ , Rb^+ and Ba^{2+} . The width of the upper core bands of crystals in a simplified scheme (Fig. 1.8) is put 3 eV. The scheme allows detection of possible superimposed luminescence bands, illustrated by an example of Cs^+ ions, incorporated into various crystal structures: rock salt, fluorite and perovskite. As mentioned before, the form of luminescence spectrum depends on the partial contribution of various (s , d) cationic states to orbitals of the valence band [1.73]. In crystals with the coordination number n for cation equal to 6, there is only the ($s - p$) hybridization of A^+ and X^- ions. That is why crystals with the rock salt lattice RbF , CsF , KF ($n = 6$) have one luminescence band. At $n = 8$ (structure of fluorite and CsCl) $s - p$ and $d - p$ hybridization of states of A^+ and X^- ions occurs, that is why luminescence spectra of BaF_2 , CsCl and CsBr crystals have two or more maxima (in CsBr at low temperatures four maxima of RL are detected).

Fig. 1.9 presents RL spectra of $\text{RbCl}:\text{Cs}$, $\text{SrCl}_2:\text{Cs}$ and $\text{RbCaCl}_3:\text{Cs}$ crystals [1.43]. In $\text{RbCl}:\text{Cs}$ crystals cesium ions replace rubidium ions, the coordination number n for Cs^+ is 6, that is why RL spectrum has one band ($\tau = 1.0 \pm 0.1$ nsec). The same case is observed for a $\text{KCl}:\text{Cs}$ crystal [1.75]. In a $\text{SrCl}_2:\text{Cs}$ crystal the transitions ($5p$, Cs) \rightarrow ($3p$, Cl) yield two maxima, because $n = 8$ ($\tau \sim 3.0$ nsec). Both matrices RbCl and SrCl_2 do not possess intrinsic CV-transitions, while the CV luminescence in $\text{RbCl}:\text{Cs}$ and $\text{SrCl}_2:\text{Cs}$ crystals has a higher intensity.

In crystals with the perovskite-type structure $n = 12$ for an A^+ ion and for a replacing ion of a univalent metal. Luminescence of $\text{RbCaCl}_3:\text{Cs}$ crystal ($\tau = 2.1 \pm 0.1$ nsec) takes a wide spectrum band (curve 3, Fig. 1.9). Besides, if more than 4 % of Rb^+ ions are replaced by Cs^+ ions, the RL output in $\text{RbCaCl}_3:\text{Cs}$ is higher than RL yield of CsCl . Thus, CV transitions of the type ($5p$, Cs) \rightarrow ($3p$, Cl) in $\text{RbCaCl}_3:\text{Cs}$ yield a higher RL output than in CsCl , because there are better conditions for the holes to enter the upper core ($5p$, Cs) band of the compound. *Thus, for one type of the transitions, by varying the composition of the radiative cluster $[\text{CsCl}_6]$, $[\text{CsCl}_8]$, $[\text{CsCl}_{12}]$ different spectra, light outputs and decay times can be obtained.*

A $\text{KYF}_4:\text{Rb}$ crystal has RL output in the range 140 - 190 nm at the level of barium fluoride [1.55]; in this case the output of intrinsic CV-luminescence of KYF_4 is lower (Table I.3). Impurity CV transitions were studied also in crystals of $\text{SrF}_2:\text{Ba}$.

A significant increase of energy yield can be expected in crystals with overlapped upper core bands. In this case the cation involved in a CV transition belongs to the chemical formula of the compound (is not an impurity). The overlapped bands should improve the conditions of "floating up" of the holes in the upper core band, that will lead to a larger share of the core holes involved in CV transitions. Investigations in this fields have just been started.

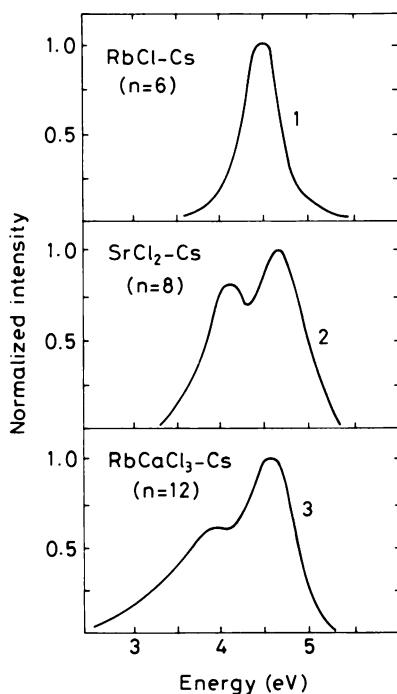


Fig. 1.9. X-ray luminescence spectra of RbCl:Cs, SrCl₂:Cs, RbCaCl₃:Cs crystals at 295 K.

It follows from the scheme presented in Fig. 1.8 that the overlapping of the following core bands: (*5p*, Cs) - (*4p*, Rb), (*4p*, Rb) - (*5p*, Ba), (*5p*, Ba) - (*3p*, K), etc. is possible. The first one of these bands (the upper one) can be called an active CV band, the second one is a transport band that ensures delivery of additional holes to the upper core band. Of special interest are crystals with the elpasolite-type structure, Cs₂RbLaF₆, Cs₂RbAlF₆, Rb₂KGaF₆. First communications that report studies of CV transitions in

crystals with the elpasolite structure: K_2LiGaF_6 , K_2NaAlF_6 [1.55] and $Cs_2NaLaCl_6$ have been published [1.76].

Fig. 1.8. shows also *d*-ion bands. The ions with the outermost *d*-shell are not CV active, however, they can form transport core bands. Then, such crystals as K_3InF_6 , K_3GaF_6 and K_3TlF_6 should be regarded as promising compounds. This point should be studied both experimentally and theoretically.

1.3. Conclusions

Anion excitonic luminescence in most halides has a low intensity at room temperature. Temperature quenching results in an increase in intensity and luminescence decay time. That is why some crystals with quenched excitonic luminescence, such as CdF_2 , can be used as fast scintillators.

Alkaline-earth fluorides are prominent among halide crystals. In these fluorides excitonic luminescence is quenched starting from temperatures slightly over room temperature. CaF_2 , SrF_2 , BaF_2 crystals possess high light outputs at room temperature but they have large luminescence decay times (hundreds nanoseconds), which can be reduced by incorporation of various impurities, RE ions in particular. The light output, however, is reduced as well.

Crystals with core-valence transitions are most proper for employment as scintillators of nano- and subnanosecond bands. Their certain advantage is a high thermal stability of all luminescence parameters. According to estimations, energy yield of luminescence of CV scintillators hardly exceeds the value of the order of 1%.

Employment of multicomponent fluoride materials allows control of parameters of both excitonic and core-valence luminescence. An increase in light output can be expected in crystals with overlapping upper core bands. A cluster character of core-valence transitions suggests that they should be sought and studied in such optical media as glasses and optical ceramics.

A high light output at short luminescence decay times can be obtained in crystals in which both excitonic and core-valence transitions, as well as other kinds of fast luminescence, occur.

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