

Scintillation mechanisms and limiting factors on each step of relaxation of electronic excitations

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Scintillation mechanisms in insulating materials are described in the general case of a simple electronic band structure and in special cases of most interest for applications: rare earth containing crystals and cross-luminescent materials with a more complicated electronic band structure. At each of the three main steps of the energy relaxation, namely (i) creation of electronic excitations, (ii) transfer to luminescent centers, (iii) emission of luminescent centers, factors limiting the performance of the scintillators are identified and the related processes described.

1. Introduction

Scintillating materials are ideal devices for detecting elementary particles and for measuring their parameters. Therefore, they are playing a major role in the development of modern nuclear physics. Scintillators are of most importance as well for other applications, in particular in nuclear medical imaging. Depending on the particular requirement of a given application, different scintillators will be preferred. Among the desirable properties of a good scintillator, high efficiency, fast scintillation and good energy resolution are of most interest in a number of cases.

Optimization of scintillating materials can be obtained only after a good understanding of the scintillation mechanism. In this paper, we propose to focus our attention on scintillation in inorganic crystalline media. Scintillation

mechanisms will be described in the general case and in two other special interest cases: rare earth containing crystals and cross-luminescent materials. Limiting factors at each step of the energy relaxation will be identified and discussed.

2. Scintillation mechanisms

The relaxation of electronic excitations involves complex mechanisms which can be simply described using schemes the electronic band structure of the crystal [1]. In a general scheme (Fig. 1), a core level, the valence band and the conduction band separated by the band gap are represented, with the time scale in abscissa and the energy in ordinate. After high energy excitation, for example by an X-ray or γ -ray photon, a deep core hole and a

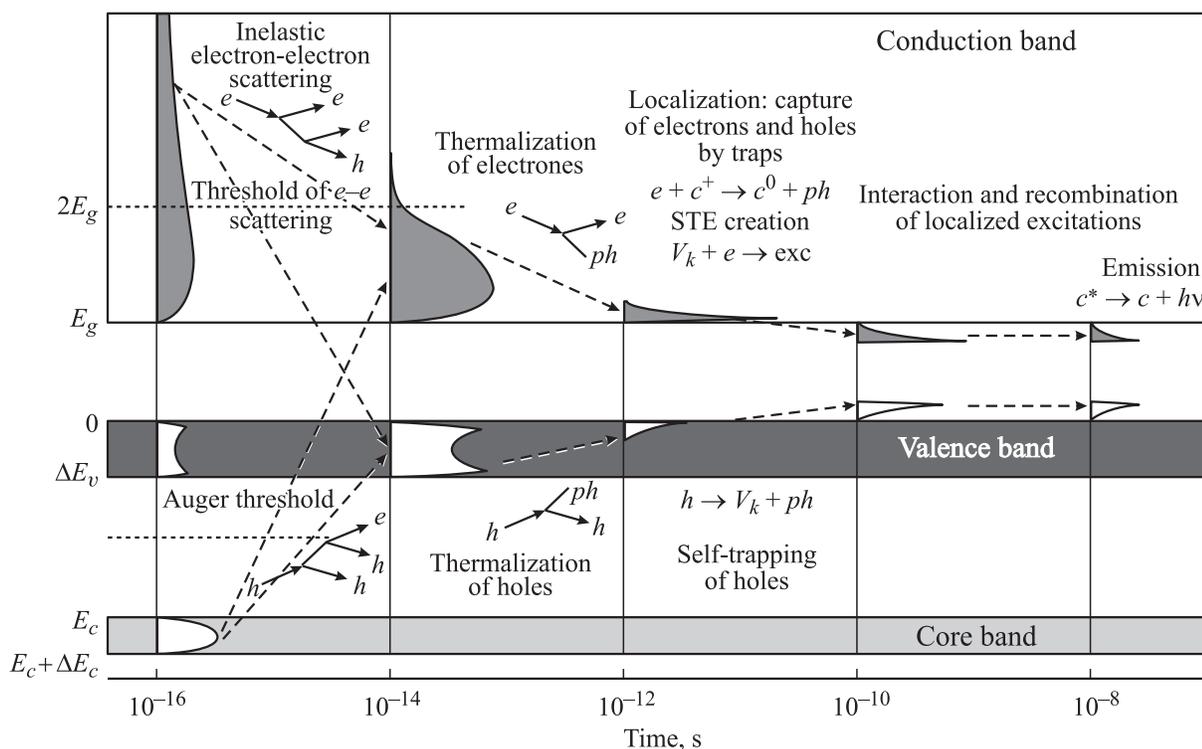


Figure 1. General scheme of relaxation of electronic excitations in an insulating material.

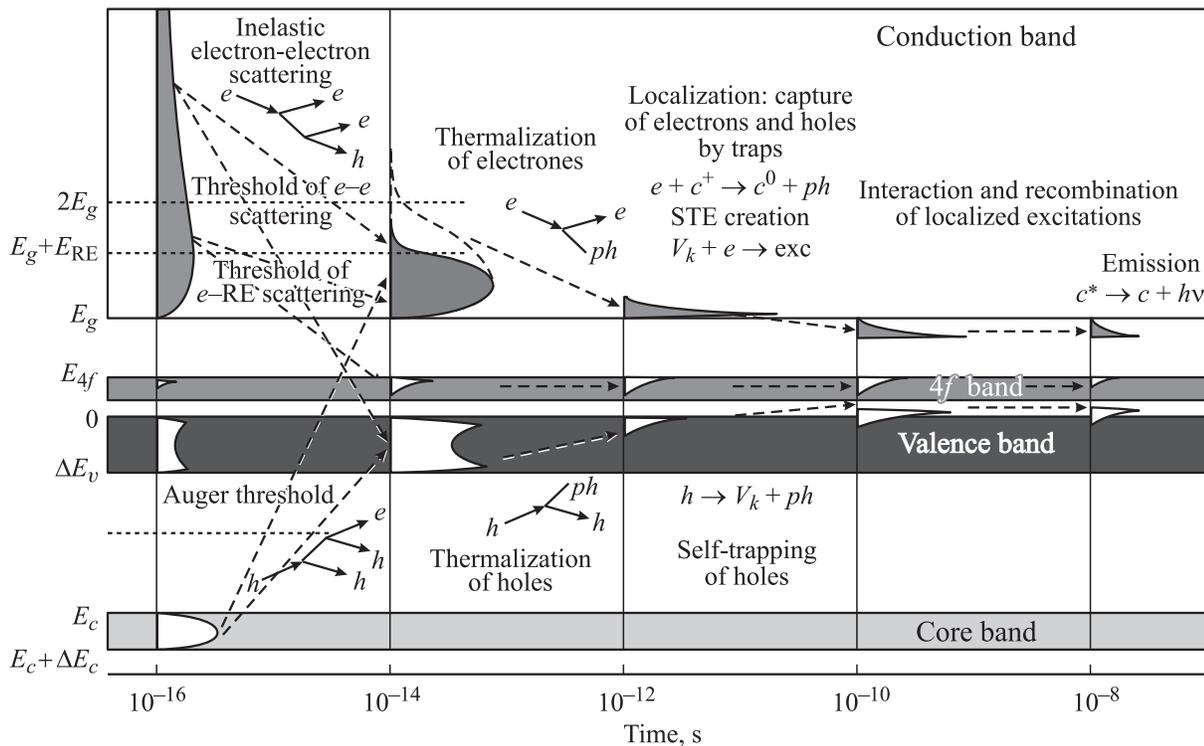


Figure 2. Relaxation of electronic excitations in rare-earth containing crystals.

hot electron are produced. The first stage of relaxation of the electronic excitation occurs at a very short time through inelastic electron-electron ($e-e$) scattering and Auger processes, leading to the multiplication of electronic excitations. Multiplication is stopped when the energy of electrons and holes becomes below the threshold of $e-e$ scattering and Auger relaxation. The second stage is dealing with the thermalization of electrons and holes with production of phonons. At the end of this stage, all the electrons are at the bottom of the conduction band and all the holes are at the top of the valence band. Then localization of excitations may arise with formation of self-trapped excitons and self-trapped holes, capture of electrons and holes by traps, etc. As a result, these centers have localized states located in the band gap. After interaction and recombination of localized excitations (fourth stage), centers may emit photons (luminescence final stage).

In many cases, strong luminescence is obtained by crystals containing luminescent ions like rare-earth (RE) ions. In this case (Fig. 2), the scheme must involve the $4f$ band of rare earth located in general in the band gap. During the first stage of relaxation, excitation of the RE ions can be obtained through electronic impact. The probability of such excitation is significant only when the electron has kinetic energy below the threshold of $e-e$ scattering and, of course, above the threshold of $e-RE$ scattering. So, rare earth excited centers can be obtained very early. An additional channel of excitation of RE is possible later on, after the thermalization stage, through sequential capture of holes and electrons by RE. The last stage involves radiative

recombination of luminescent centers, and in particular of RE centers.

Another interesting case is cross-luminescent crystals. Cross-luminescence is due to a radiative electronic transition from the valence band to the uppermost core band, providing the Auger relaxation of the uppermost core band hole is strictly forbidden. This situation occurs when the energy difference between the uppermost core level and the valence band is less than the band gap. The archetype of cross-luminescent crystals is BaF_2 . Such crystals give rise to very short sub-nanosecond luminescence decays which can be of interest for some applications. Unfortunately, the light yield is usually relatively weak because only a few number of excitations created in the crystal are useful to produce cross-luminescence. To describe the relaxation of excitations, it is therefore necessary to involve the uppermost core band in the scheme [1].

3. Limiting factors at each step of the energy relaxation

It is well known that the scintillation efficiency η can be described as the product of three terms, each one representing a step in the energy relaxation:

$$\eta = N_{eh}SQ, \quad (1)$$

where N_{eh} is the conversion efficiency (number of electron-hole ($e-h$) pairs or excitons), S is the probability of transfer to emitting centers, Q is the luminescence quantum yield.

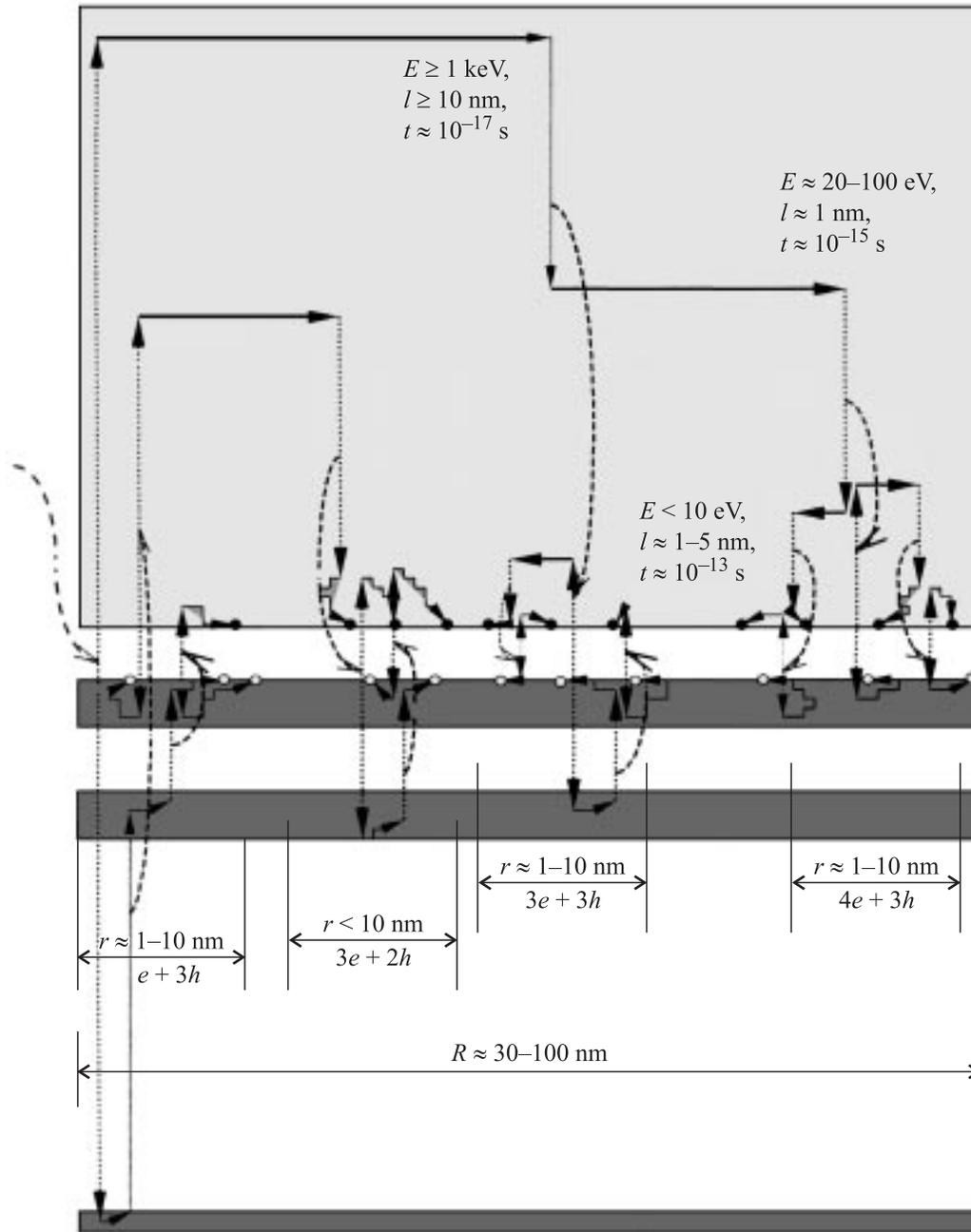


Figure 3. Clusters of closely-spaced electronic excitations created in insulating crystal after excitation by a high energy particle.

3.1 First step: creation of electronic excitations. The number of $e-h$ pairs can be written as

$$N_{eh} = E_{inc}/E_{eh},$$

where E_{inc} is the energy deposited by an ionizing particle and E_{eh} is the average energy required for the creation of a thermalized $e-h$ pair.

A general accepted estimation of E_{eh} is around $(2-3)E_g$ (E_g is the forbidden energy bandgap) for a simple case represented in Fig. 1 [2,3]. So, E_g is a limiting factor for the production of $e-h$ pairs and excitons.

However, N_{eh} is a relevant factor only in the case of a simple insulator for which thermalized electrons and holes are the only types of electronic excitations and E_g the only parameter characterizing the conversion efficiency. We have seen that it is not the case of scintillators with core-valence transition. For example, in BaF_2 , the relevant factor is not N_{eh} but the number of uppermost $Ba^{2+} 2p$ core holes. In the case of cerium compounds, for example CeF_3 , two types of exciton coexist: Ce Frenkel and anion Wannier excitons. It was shown that cerium excitation is not efficient, either through energy transfer from anion exciton [4,5] or

through sequential capture of holes [6]. Useful excitations can be produced efficiently only through impact excitation and as indicated in Fig. 2 by electrons with kinetic energies in a narrow band between the two thresholds of $e-e$ scattering and of $e-RE$ scattering. As a result, the number of useful excitations is reduced by a factor around 5 in CeF_3 , explaining its relatively low light yield.

3.2. Second step: transfer to luminescence centers. This is a very critical part of the scintillation mechanism.

For high light yield scintillators, the transfer to luminescence centers occurs essentially through sequential capture of charge carriers. It is for example the case for Na- and Tl-doped CsI. In the case of Ce^{3+} -doped or -based crystals, a limiting factor is the energy difference ΔE between the $Ce4f$ level in the forbidden bandgap and the top of the valence band. In oxides and halides, ΔE is weak and the cross-section for hole capture may be high. In fluorides, ΔE is large and the hole capture probability is never high [6].

Impurity ions can compete with active ions for the capture of charge carriers and/or interact with them, and can therefore induce severe limitations in scintillation efficiency. For example, in cerium-doped or cerium-based crystals, in general the presence of metal ions M^{n+} with two or more stable valence states is harmful. Charge transfer may occur between M^{n+} and Ce^{3+} according to the following process: $(Ce^{3+}, M^{n+}) \rightarrow (Ce^{4+}, M^{(n-1)+})$. Furthermore, M^{n+} ions may act as traps for charge carriers. It is known that the presence, along with Ce^{3+} , of ions like Yb^{3+} , Eu^{3+} , W^{6+} , V^{5+} most often kill the Ce^{3+} fluorescence. It was shown that the presence of Ir^{4+} in $Lu_2Si_2O_7 : Ce^{3+}$ strongly quenches the scintillation of this crystal [7]. The coexistence of Ce^{4+} with Ce^{3+} is harmful as well because Ce^{4+} is an efficient electron trap and does not lead to charge transfer luminescence.

Self-trapping can strongly influence the efficiency and the time-dependence of the scintillation, in particular creation of self-trapping holes (V_k centers) and self-trapped excitons (STE). Energy transfer is very fast through direct correlated $e-h$ capture, while it is fast through binary $e-h$ recombination $V_k + e^-$ on scintillation center and much longer through STE diffusion.

Trapping effects on the scintillation may be very spectacular. It is the case in $YAG:Yb^{3+}$ where the charge transfer luminescence is strongly quenched at low temperature where glow peaks arise reflecting the presence of traps. At temperature of these peaks, a long component in the fluorescence decay profiles is observed due to de-trapping and re-trapping processes [8].

Closely-spaced electronic excitations can be formed in an insulator after high energy excitation [9,10]. It is due to the fact that the mobility of holes is much smaller than the mobility of electrons. Formation of a cluster of electronic excitations is illustrated in Fig. 3. Interactions between closely-spaced electronic excitations may lead to a substantial decrease of the number of correlated and non-correlated $e-h$ pairs and consequently of the light yield of

the scintillator. For example, an exciton may disappear after interaction with a close low energy electron or hole; a core hole may interact with a low energy electron or a valence band hole and no more excitations are created [10].

3.3. Third step: emission of scintillation centers. Many processes may limit the luminescence efficiency, and most of them are well-known: (i) electron-phonon coupling resulting in a competition between radiative and non-radiative transitions; (ii) concentration quenching due to interaction between luminescence centers; (iii) reabsorption process where the luminescence travelling through the scintillator can be reabsorbed either by identical or by unlike centers; (iv) photo- and thermal-ionization quenching processes.

These latter processes can be illustrated through two examples.

3.3.1. Electron ionization in cerium-doped crystals. The location of the lowest $5d$ emitting state may be close or degenerated in the conduction band. It was demonstrated that the autoionization rate from a $5d$ state is large in many cases [11–13] and the delocalization of the electron may lead to the quenching of the luminescence. Photoionization process is an important limiting factor for the light yield.

When all the $5d$ states are degenerated in the conduction band (the case of Ce-doped sesquioxides La_2O_3 , Y_2O_3 , Lu_2O_3), the onset of the room temperature and liquid nitrogen-temperature photoconductivity coincides with the onset of the lowest absorption band and the cerium emission is totally quenched [14].

When the lowest $5d$ state is close to the conduction band, thermal quenching is governed mainly by thermo-stimulated ionization (Fig. 4). For Ce-doped Lu_2SiO_5 scintillator, ΔE is few tenths of eV, and efficient emission is observed even at room temperature. But the light yield strongly decreases for T above the room temperature. For Ce-doped $LaAl_3$, $\Delta E < 0.1$ eV, no emission is detected at room temperature; efficient emission is only detected at $T < 100$ K [15].

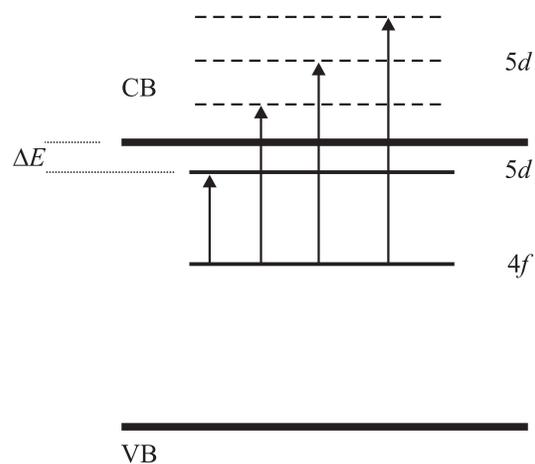


Figure 4. Thermo-stimulated ionization process in cerium-doped crystals.

Of course, when the lowest $5d$ state is well below the conduction band, photoionization process does not occur. It is the case of most Ce-doped fluorides, chlorides and oxides. Thermal quenching is then governed by non-radiative relaxation to the ground state. High luminescence efficiency can be exhibited at high temperature by some scintillators like $\text{LuAlO}_3 : \text{Ce}^{3+}$ and $\text{Lu}_2\text{Si}_2\text{O}_7 : \text{Ce}^{3+}$.

3.3.2. Hole ionization in ytterbium-doped crystals. The temperature dependence of the charge transfer and IR luminescence yield under excitation in the charge transfer (CT) band (Fig. 5, *a*) shows that the feeding of $^2F_{5/2}$ and $^2F_{7/2}$ states through radiative and non-radiative transitions from the CT state (Fig. 5, *b*) can explain both CT and IR luminescences thermal dependence for $T > 150\text{ K}$, but not the behavior of the IR luminescence at lower temperature. Another quenching mechanism must be involved. After taking into account hole ionization with formation of CT state after thermal dissociation, a good simulation of the IR luminescence at low temperature is

obtained. It seems that the dominant thermal quenching process of CT luminescence in most of Yb^{3+} -doped oxide systems could be due to hole thermo-stimulated ionization from the charge transfer state [16].

4. Conclusions

Scintillation mechanisms were described using simple schemes deduced from appropriate models. Multiplication of electronic excitations is described using kinetic equations. Modelling of energy relaxation is performed using Monte Carlo technique describing the thermalization, separated diffusion and spatial correlation of electronic excitations.

It was shown that a good estimation of the light yield can be obtained providing to take into account some considerations, like the fact that created electronic excitations are not all useful excitations in systems with complicated band structure, and that clusters of closely-spaced electronic excitations can be formed.

Many limiting factors for the light yield and the time dependence of the scintillation must be considered at each stage of the energy relaxation.

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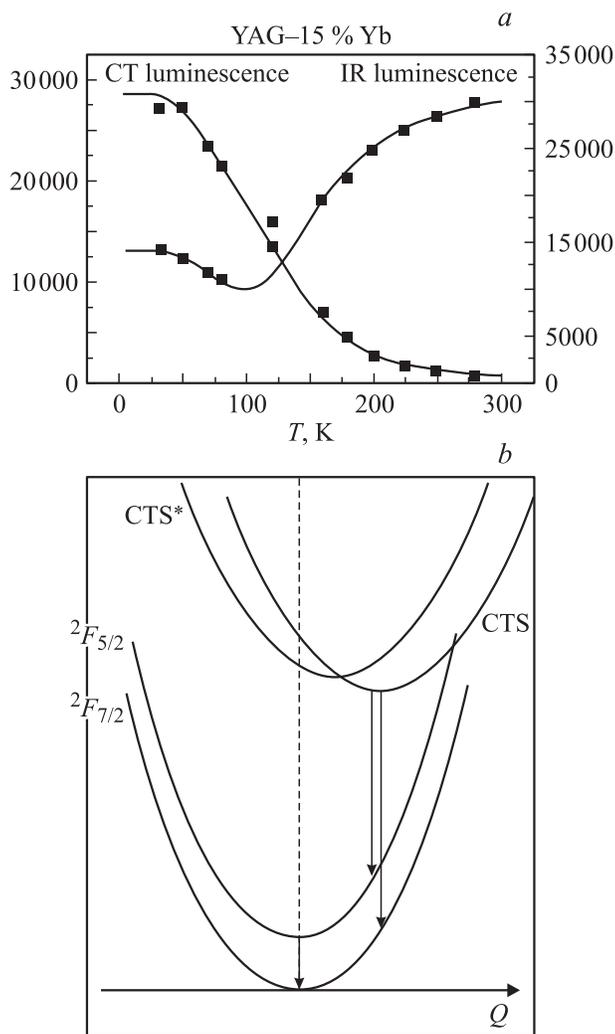


Figure 5. (*a*) Temperature dependence of the charge transfer and IR luminescence yield under excitation in the CT state (6.2 eV); (*b*) CT states and emission transitions.