Experimental study of the excitation threshold of fast intrinsic luminescence of CsI

A. N. Belsky, A. N. Vasil'ev, and V. V. Mikhailin
Synchrotron Radiation Laboratory, Physics Department, Moscow State University, 119899 Moscow, Russia

A. V. Gektin
Institute for Single Crystals, 310141 Kharkov, Ukraine

P. Martin
*Laboratoire pour l'Utilisation du Rayonnement Electromagnetique, Centre National de la Recherche Scientifique,
Bâtiment 209D, Centre Universitaire Paris-Sud, 91405 Orsay Cedex, France
and Centre de Recherches Nucléaires, 23 rue du Loess, 67037 Strasbourg Cedex, France*

C. Pedrini and D. Bouttet
*Laboratoire de Physico-Chimie des Matériaux Luminescents, Université Lyon I, Bâtiment 205, 43, boulevard du 11 Novembre 1918,
69622 Villeurbanne Cedex, France*
(Received 8 October 1993)

A type of intrinsic luminescence in crystals has been revealed. The excitation threshold of well-known fast intrinsic luminescence of CsI (300 nm band) has been obtained from the excitation spectrum measured in the photon-energy range 5–125 eV at 300 K using synchrotron radiation. The excitation starts from an energy of about 20 eV and exponentially increases up to the $4d$ I^- ionization energy (~ 50 eV). Such high-energy broad threshold is not typical for any conventional mechanisms of luminescence excitation. We attribute this type of luminescence to the emission center, which is created by the interaction of several elementary excitations produced in the process of relaxation of a primary excitation. The possible role of $4d$ I^- core levels is discussed. The nanosecond decay kinetics of this luminescence is nonexponential for all energies of excitation.

I. INTRODUCTION

The quantum yield of most of the known types of luminescence in the region of excitation photon energies $h\nu = (6-8)E_g$ (E_g is the forbidden gap of the crystal) cannot exceed the quantum yield for the low-energy region of the fundamental absorption $h\nu \approx E_g$ or for direct excitation of the luminescent center by more than three- to fourfold. This is valid for the luminescence of impurity centers, free or self-trapped excitons, and other luminescent centers either stationary or created by photons with the energy of about E_g. The exception is the cross-luminescence, the nature of which is similar to that of x-ray fluorescence. This type of luminescence is observed in crystals with an excitation energy for the upper core band less than two forbidden gaps, which is not valid for CsI. The excitation threshold of the cross-luminescence is the onset of the transitions from the upper core cation level (e.g., $5p$ Ba^{2+} in BaF_2, $5p$ Cs^+ in CsCl, etc.) and the threshold region is rather narrow (about 1 eV).[1]

Fast intrinsic luminescence (FIL) of CsI was observed at room temperature 30 years ago.[2] The properties of this emission were intensively studied by different groups due to good scintillation characteristics of this emission.[3-5] Nevertheless, the mechanisms of this luminescence is not established yet.

The specific feature of FIL is its high efficiency under γ- and x-ray excitation (energy yield is about 1% for 1 keV x-rays[3]) and a zero yield (or a very low yield) in the region up to 30 eV.[6] This unusual property of the emis-

sion together with fast nonexponential kinetics of the luminescence decay after x-ray excitation[7] makes FIL of CsI different from other well-known types of emission observed in ionic crystals. The establishment of the threshold of the CsI FIL excitation and the study of its properties in the vicinity of this threshold seem to be very helpful to clarify the origin of these processes in crystals.

II. EXPERIMENTAL PROCEDURE

The measurements were carried out at the SuperACO positron storage ring of LURE, France. The normal incidence monochromator with 3 m toroidal holographic grating with 300 lines/mm at the beam line SA61 allowed to excite crystals by photons 4–40 eV, whereas the grazing incidence monochromator with a 2.2 m toroidal grating with 1200, 1800, and 2400 lines/mm at the beam line SA71 was used to excite crystals by photons 22–125 eV. The FIL through interference filters was detected by a PM-9789. The excitation spectrum of sodium salicylate was used as a reference. The time-to-pulse converter and multichannel analyzer (150 ps/channel) were used for time-resolved experiments.

III. EXPERIMENTAL RESULTS AND DISCUSSION

A. FIL excitation spectrum

The FIL excitation spectrum measured at 300 K (Fig. 1) starts from the energies about 15–20 eV and gradually increases with the energy. The FIL efficiency for the ex-
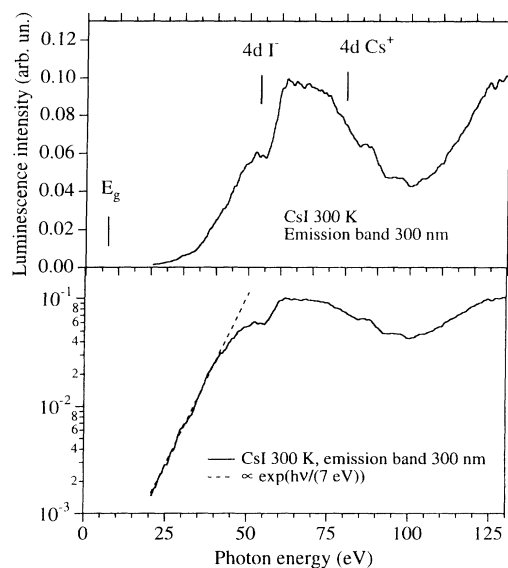
FIG. 1. Excitation spectrum of the FIL of CsI (interference filter 300 nm) measured at 300 K (top panel) and in semilogarithmic scale (bottom panel) and exponential fitting of the starting region (dashed line).

FIG. 2. Excitation spectra of CsI luminescence: the FIL (300 K) (thick) and of triplet exciton (100 K) (thin) compared with CsI absorption (dashed).

citation region above 50 eV is rather high, so the threshold definitely lies below this energy. The spectrum of the FIL has a doublet minimum at 53 and 55 eV corresponding to $4d_{3/2} \rightarrow 5p$ and $4d_{5/2} \rightarrow 5p$ transitions in I^- (the position of which are slightly shifted from that in atomic spectra[8]) and reaches the maximum at energies about 60 eV. The yield of FIL at this energy is comparable with that after x-ray excitation. The features of the excitation spectrum at the energies corresponding to the threshold of $4d$ Cs^+ core-level ionization and above (70–120 eV) are inverse to those of the absorption spectrum of Cs^+ ions in cesium compounds.[9] This effect of anticorrelation of the quantum yield and absorption coefficient is often displayed in excitation luminescence spectra in the VUV region[10] and is attributed to the effect of surface losses.[11,12] The detailed analysis of the FIL excitation in this region requires the knowledge of the absorption coefficient for CsI where the transitions from $4d$ I^- and $4d$ Cs^+ core states overlap.

The CsI FIL excitation starts at energies where the multiplication of electronic excitations with the production of secondary excitations becomes possible.[13] The multiplication threshold in CsI for processes of the production of secondary excitons and/or low-energy electron-hole pairs should be about $(2-3)E_g$, i.e., 12–18 eV.

The essential difference in the excited state of the crystal created by photons of the energies below and above the multiplication threshold is that the spatial distribution are quite different in these two cases. The types of excitations are the same in both cases, but when two excitations are created in the process of inelastic scattering, the distance between them is quite small as is defined by the mean free path of the high-energy excitation and is
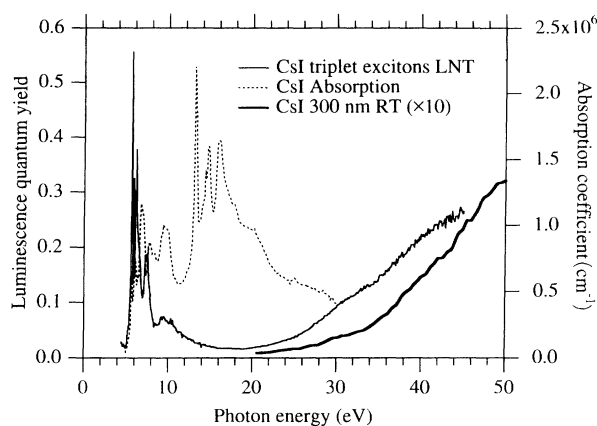
about 1–10 nm. Thus two excitations are created in correlated positions. On the other hand, the absorption of two photons is noncorrelated, so the mean distance between excitations created by two different photons with lower energies is determined by the intensity of the excitation I, mean lifetime τ, and absorption coefficient k and is about $(I\tau k)^{-1/3}$. This distance is much larger than 100 nm for typical excitation intensities.

Let us compare the CsI FIL excitation spectrum (thick curves in Fig. 2) with that of triplet exciton emission in the same crystal (thin curve), the behavior of which is typical for one of the conventional mechanisms of excitation. The luminescence of triplet excitons is excited well in the exciton absorption region (about 6 eV), and its efficiency strongly decreases at higher energies. This decrease is connected with the increase of the separation between an electron and a hole created by a vacuum ultraviolet photon.[14] The fine structure is connected with the surface losses (compare the absorption spectrum, dashed curve, with the triplet luminescence yield, thin one). In the multiplication region the mean electron-hole separation decreases again and thus the increase of the yield is expected. Nevertheless, the increase is rather slow and the efficiency of the production of several triplet excitons by a single absorbed photon due to the inelastic scattering of the primary electron becomes substantial only at the energies about 35 eV. The comparison shows the essential difference in the excitation spectra. The FIL excitation spectrum flatly starts above $(2-3)E_g$, and only in the region of the prominent interaction of secondary excitations is its profile, to a great extent, similar to that for triplet excitons in the energy region 20–35 eV. Nevertheless, the absolute values of the quantum yield of the triplet exciton emission are much higher than that of FIL at these energies.

Thus the analysis of the FIL excitation spectrum in the threshold region brings us to a conclusion that the creation of two or more correlated excitations is of essential importance in the processes resulting in the FIL of CsI.

B. Excitation edge

The efficiency of the creation of such correlated excitations (both stationary or nonstationary) becomes higher after the excitation of inner core electrons. The distance between two excitons is quite small if they are produced by the Auger decay of the core hole at the $4d$ I^- level. This decay results in two holes in the valence $5p$ I^- band, and the probability that these holes are at the same ion or at the neighbor ions is rather high. The double ionization of iodine atoms by a photon whose energy corresponds to the $4d$ ionization energy has been shown recently.[15]

Let us return to the FIL excitation spectrum [Fig. 1 (bottom panel)]. The excitation edge of the FIL can be fitted by the exponential curve [$\propto \exp(-h\nu/E_0)$] with the typical energy $E_0 \approx 7$ eV. This profile of the excitation edge cannot be explained in an unambiguous manner. Its exponential behavior can be connected not only with the increase of the number of correlated excitations after the inelastic scattering but can have an additional origin connected with the Auger decay of $4d$ I^- hole. Nevertheless, one should suppose that the Auger decay of $4d$ I^- hole starts at lower energies.

This hypothesis can be justified in the following way. It is well-known that the Urbach tail of the near-exciton absorption is exponential. One of the reasons for such an Urbach tail is the multiparticle interaction of the exciton state with optical phonons in the crystal, i.e., interaction with boson field. The characteristic energy E_U of the Urbach law [$\exp(-\sigma h\nu/E_U)$] is the optical phonon energy, σ is in the region $0.5-2$. For our case of the $4d$ core exciton or hole, the interaction with another boson field is possible, i.e., with valence band excitons ($E_{ex} = 6$ eV). The excitation spectrum of the FIL at the energies below the $4d$ I^- ionization energy should be proportional to the Urbach-like tail of absorption. In this case the characteristic energy E_0 of the exponential law of the excitation is about exciton energy E_{ex}. Such long tails of absorption below the threshold energies are well known in the x-ray appearance near-edge structure (XANES) region for deep core levels (but the reasons of the tails are not discussed in most articles).

C. Nature of FIL center and decay kinetics

We can make only suppositions about the structure of the FIL emission center created by correlated excitations. This center is the result of phonon relaxation of correlated excitations. The simplest supposition is the creation of free or self-trapped biexciton. The alternative one is the creation in this high excited region of crystal of specific type of radiation defect, e.g., cation vacancy. Some features of these centers are displayed in FIL kinetics (Fig. 3).

The kinetics of the FIL of CsI definitely cannot be fitted by a single or double exponential function. It is fast (typical time shorter than 1 ns) in the initial part and becomes slower at the final stages. This fact displays that the nonradiative decay of luminescent centers is important at the initial stages of relaxation. Nevertheless, the
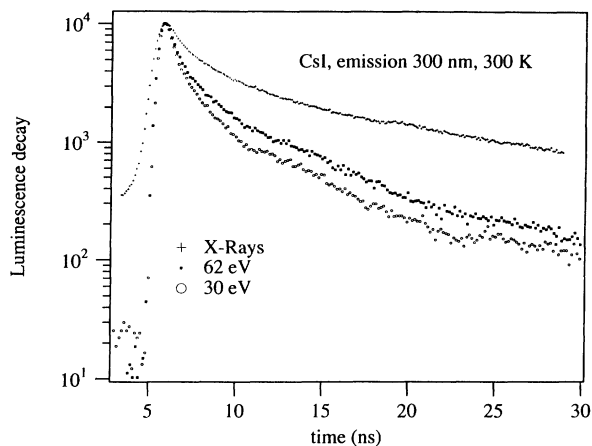

FIG. 3. Decay curves of FIL of CsI excited by 30 and 62 eV photons compared with x-ray excitation (Ref. 3).

asymptotic behavior can be fitted by exponential law with a typical time about 20 ns. This time can serve as the radiation time of the FIL emission centers.

The decay kinetics is faster for low energy of the excitation and becomes slower for the excitation at the maximum of the efficiency of excitation (62 eV). For energies below and above this energy the kinetics lies between the curves of 30 and 62 eV shown in Fig. 3. For x-ray excitation the kinetics is sufficiently slower than for vuv excitation. The displayed kinetics differ in the initial region. The difference in the initial stages may be due to nonradiative relaxation processes between these centers and other excitations. The examination of these differences will give the opportunity to extract the information about the spatial distribution of electronic excitations in the excited region.

IV. CONCLUSION

A type of intrinsic luminescence in crystals has been revealed. The excitation threshold, which is several times larger than the forbidden gap, was observed for fast intrinsic luminescence of CsI. The peculiarity of its excitation edge is the exponential growth. These facts allow us to suppose that there exists a type of luminescence center created only by a high-energy photon. The main feature of this phenomenon is that the centers are created as the result of the strong interaction of hot excitations. Thus the observation of such a threshold is also important for examination of the dynamics of excited regions created in a crystal by a high-energy photon, since all proposed models are connected with the strong interaction of close excitations created by a single photon. Therefore, the kinetics of such luminescence can be a probe for the dynamical distribution of electronic excitation at the primary stages of relaxation.[16] The consideration allows one to suppose that these processes are rather general and such processes can be observed in some other crystals.

ACKNOWLEDGMENTS

[1] V. N. Makhov, Nucl. Instrum. Methods Phys. Res., Sect. A **308**, 187 (1991).

[2] T. Towyama, I. Morita, and M. Ishiguro, J. Phys. Soc. Jpn. **25**, 1133 (1968).

[3] V. V. Gavrilov, A. V. Gektin, N. V. Shiran, and T. A. Charkina, Opt. Spektrosk. **66**, 961 (1989).

[4] S. Kubota, S. Sakuragi, S. Hashimoto, and J. Ruan, Nucl. Instrum. Methods Phys. Res., Sect. A **268**, 275 (1988).

[5] C. L. Woody et al., IEEE Trans. Nucl. Sci. **NS-37**, 492 (1990).

[6] A. N. Belsky, A. N. Vasil'ev, V. V. Mikhailin, A. V. Gektin, N. V. Shiran, A. L. Rogalev, and E. I. Zinin, Rev. Sci. Instrum. **63**, 806 (1992).

[7] A. V. Gektin, N. V. Shiran, A. N. Belsky, and A. N. Vasil'ev, Nucl. Tracks Radiat. Meas. **21**, 11 (1993).

[8] L. Nahon and P. Morin, Phys. Rev. A **45**, 2287 (1992).

[9] M. Kamada, O. Aita, K. Ichikawa, M. Okusawa, and K. Tsutsumi, Phys. Rev. B **45**, 12 725 (1992).

[10] A. N. Belsky, I. A. Kamenskikh, V. V. Mikhailin, I. N. Spinkov, and A. N. Vasil'ev, Phys. Scr. **41**, 530 (1990).

[11] Ch. Ackermann, R. Brodmann, U. Hahn, A. Suzuki, and G. Zimmerer, Phys. Status Solidi B **74**, 579 (1976).

[12] M. A. Elango, V. N. Kadchenko, A. M.-E. Saar, and A. P. Zhurakovskiy, J. Luminescence **14**, 375 (1976).

[13] V. V. Mikhailin, Nucl. Instrum. Methods Phys. Res., Sect. A **261**, 107 (1987).

[14] A. N. Vasil'ev and V. V. Mikhailin, Bull. Acad. Sci. USSR Phys. Ser. **49** (9), 164 (1985).

[15] L. Nahon, P. Morin, and F. Combet-Farnoux, Phys. Scr. **41**, 104 (1992).

[16] A. N. Belsky, I. A. Kamenskikh, V. V. Mikhailin, and A. N. Vasil'ev (unpublished).