Laboratori Nazionali di Frascati

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Excitation of high energy electronic states in pure alkali halides at low temperature give rise to the intrinsic luminescence due to the radiative decay of the self-trapped exciton. The relaxation processes before the self-trapping involve the electron-electron and electron-lattice interactions[1]. These interactions have been prevalently studied by means of photoemission, reflectivity and excitation spectra of the intrinsic luminescence in the steady-state regime.

The most interesting results obtained so far are connected mainly with the relaxation of core excitations and the mechanism of "photon multiplication".

A "photon multiplication" process[2] has been supposed to take place for excitation energy at about $E_g + nE_x$ (n=1,2,...), where E_g is the energy gap and E_x is the valence exciton energy. For these energies, a depression of the photoemission yield and a "step" of the luminescence yield, that becomes higher than one, is observed.

The photoemission yield at the core excitations shows a pronounced peak even if the electron excited state is a bound state.

The explanation of these experimental results shows some contradictions. In fact, the observed results are interpreted by means of a process that involves either an elastic electron-electron scattering or an anelastic scattering of the excited electrons that give rise to various simple excitations with subsequent emission.

The core exciton $K^+ 3p$, for example, can decay either directly or by Auger effect in the continuum of the valence excitations so that electrons with different energies are present in the conduction band. The two processes are in competition and seem not associated to a lattice relaxation[3,4]. On the other hand, in alkali halides, the core excitons

line width is larger than the Auger line width and this behaviour can be explained only by assuming a strong electron-lattice interaction[5].

Time-resolved spectroscopy is a very good tool for the investigation of these decay processes. It can contribute significantly to a better understanding of the relaxation mechanisms.

Taking advantage from the good time structure of the Adone synchrotron radiation in Frascati, we have studied the time characteristics of the fast σ component (λ_{em}=2910 Å, $\Delta\lambda$=80 Å) of the self-trapped exciton luminescence in KI, detected by means of a time-correlated single photon counting technique.

A crucial point of any time resolved apparatus is the evaluation of its time resolution. In our case, we give an estimation of this resolution on the basis of the Zimmerman and Cutler method[6]. According to this method, the time resolution in a decay measurement is the apparent decay time resulting from the deconvolution procedure[7] between two exciting pulses measured immediately before and after the luminescence decay measurement. For the deconvolution we use as response function a sum or difference of exponentials, in order to put in evidence either the existence of two decay times or the existence of a growth and a decay time. The decay time resolutions obtained in sixteen observations reported in Fig. 1, group around 100 ps. In the same way we obtain a growth time resolution of a few picoseconds.
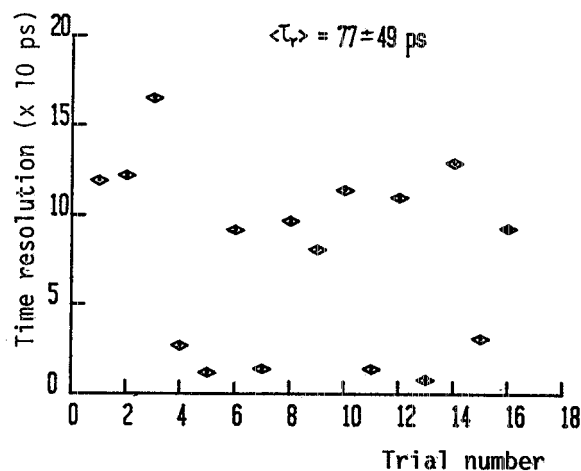

Fig. 1 - Instrumental time resolution obtained follow
ing the Zimmerman and Cutler method.

Excitations of the intrinsic luminescence have been selected at 13.5 eV (915 Å) in the first depression of the photoemission yield (E_g+E_x), at 21.2 eV (584 Å), at one of the K^+3p core excitons, and at 22.5 eV (550 Å), at about E_g+3E_x. In Fig. 2 we show an example of the σ luminescence

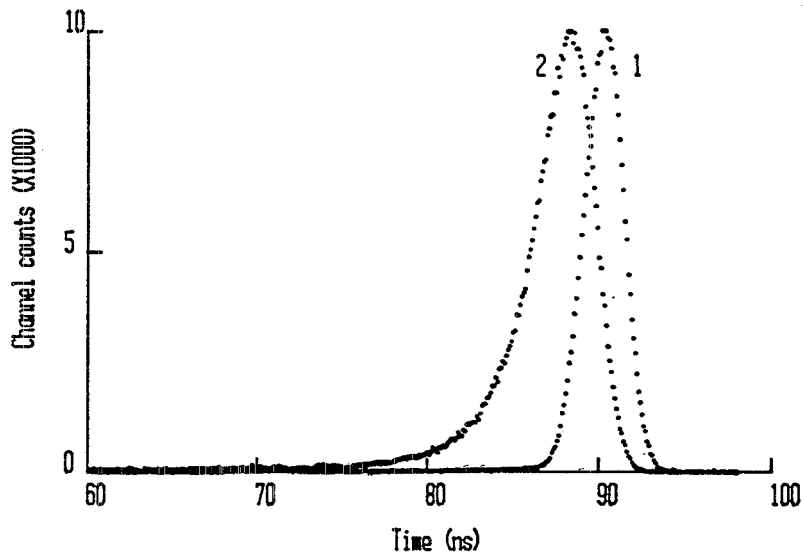decay in KI together with the excitation pulse.

Fig. 2 - Time decay spectra (inverted time scale) observed in pure KI at 50 K. 1 - Exciting pulse shape measured using the sample scattered light at the emission wavelength. 2 - Time decay of the 4.12 eV intrinsic luminescence band (λ_{em}=2910 Å, $\Delta\lambda$=80 Å) for excitation at λ_{exc}=930 Å (E_g+E_x).

The measurements were performed for temperature ranging from 15 K to 70 K.

The main results we obtain after the deconvolution of the luminescence decays are:

a) a σ luminescence lifetime of 2.30$\pm$0.07 ns that does not depend on the exciting energy and on the temperature;

b) for excitation at 13.5 eV, a growth time of 260$\pm$70 ps that does not depend on the temperature;

c) for excitation in the K^+3p core exciton, there is no growth time; at some temperatures a decay time appears of about 10-20 ns in addition to the usual decay;

d) excitation at 22.5 eV seems to show a temperature dependent growth time that becomes about 400 ps at 15 K.

While the result of point a) confirms what has been found by other authors, the other are quite new results. They give interesting informations about the dynamics of these high energy excited states. The results of points b) and d) are very interesting. In fact, the growth time of

the σ luminescence for electrons excited in the conduction band is esti-
mated to be 5-10 ps in KI at low temperatures[8]. The growth time of the
σ luminescence can be attributed to the relaxation mechanism of the exci-
tation at $E_g + E_x$ before the electron drops to the bottom of the conduction
band. Moreover, the independence on the temperature of this growth time
seems to rule out an effective electron-lattice interaction during the
relaxation. The result of point d) indicates that the electron-lattice
interaction becomes effective at higher excitation energies.

As far as the core excitation is concerned, the istantaneous growth
time of the σ luminescence suggests a relaxation path with different cha-
racteristics than that of cases b) and d). The decay time of about 10-20
ns can have the same origin as that found in ref.(9).

The results we present here need a deeper analysis to reach a more
satisfactory comprehension of the relaxation processes. Nevertheless this
work demonstrates that it is possible to have good information about the
relaxation of high energy electronic excited states in alkali halides.
For this it is necessary to perform and compare systematic decay measure-
ments of the   luminescence for excitations in the valence and core ex-
citons and in the band to band absorption.

References:

(1) G.Zimmerer, Defects in Insulating Crystals (Springer-Verlag, 1981).
(2) S.N.Ivanov et al., Sov. Phys. Solid State 15, 1053 (1973).
(3) G.J.Lapeyre et al., Solid State Comm. 15, 1601 (1974)
(4) G.J.Lapeyre et al., Phys. Rev. Letters 33, 1290 (1974).
(5) M.Iwan and C.Kunz, Phys. Letters 60A, 345 (1977).
(6) H.E.Zimmerman and J.P.Cutler, Chem. Comm. 598 (1975).
(7) A.E.McKinnon, A.G.Szabo and D.R.Miller, J. Phys. Chem. 81, 1546
    (1977).
(8) Y.Suzuki et al., J. Phys. Soc. Japan 49, 207 (1980).
(9) I.M.Blair, D.Pooley and D.Smith, J. Phys. C5, 1537 (1972).