# The Role of Activator-Activator Interactions in Reducing in Low-Voltage-Cathodoluminescence Efficiency in Eu and Tb doped Phosphors[*]

by

## C. H. Seager and D. R. Tallant

Sandia National Laboratories

Albuquerque, NM 87185

## ABSTRACT

High resolution measurements of spectrally resolved cathodoluminescence (CL) decay have been made in several commercial and experimental phosphors doped with Eu and Tb at beam energies ranging from 0.8 to 4 keV. CL emission from the lowest two excited states of both rare earth activators was compared to the decay of photoluminescence (PL) after pulsed laser excitation. We find that, at long times after the cessation of electron excitation, the CL decay rates are comparable to those measured in PL; at short times, the decay process is considerably faster and has a noticeable dependence on the energy of the electron beam. These beam energy effects are largest for the higher excited states and for phosphors with larger activator concentrations. Measurements of the experimental phosphors over a range of activator fractions from 0.1 to 0.002 show that the beam energy dependence of the steady-state CL efficiency is larger for higher excited states and weakens as the activator concentration is reduced; The latter effect is strongest for $Y_2SiO_5$:Tb, but also quite evident in $Y_2O_3$:Eu. We suggest that the electron beam dependence of both the decay lifetimes and the steady state CL

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efficiency may be due to interaction of nearby excited states which occurs as a result of the large energy deposition rate for low energy electrons. This picture for non-radiative quenching of rare earth emission is an excited state analog of the well-known (ground state-excited state) concentration quenching mechanism.

Recent demonstration of prototype flat panel field emission displays has emphasized the need for phosphors which are efficient at low electron beam energies[1-3]. Except for ZnO, which has poor chromaticity, essentially all conventional phosphors have efficiencies which decline monotonically as the electron excitation energy drops below 5 keV. Consequently most manufacturers have utilized conventional cathode ray tube phosphors excited by 4-6 keV electrons in prototype FED displays; these devices have high internal electric fields, a feature that raises device cost and complexity and introduces problems with charging of dielectric standoffs.

Conventional explanations for reduced low voltage CL efficiency usually begin with the assumption that to achieve excitation of the luminescent activators[3], beam-excited electrons and holes must recombine near to, or at these impurities, *and* that: 1. the near surface region of phosphors is highly defective, reducing the local electron-hole lifetime, or 2. Most of the excited electrons and holes actually diffuse to the surface, where they combine non-radiatively. Both 1. and 2. would be increasingly important if the primary exciting electrons have low energy and, hence, reduced range. In these scenarios, most of the crucial energy loss occurs **before** excitation of the activators. In this letter we will present both steady state and pulsed CL data which seem to show that non-radiative energy losses *after activator excitation* may be important for the phosphors that are studied here. This data also emphasizes the increasingly important role of activator interactions in quenching CL at low beam energies.

All of the CL decay measurements reported here were made on screened phosphor samples with a conventional Kimball[4] electron gun by pulsing the grid to turn the electron beam on and off. Extensive signal averaging of the spectrally filtered, photomultiplier-detected luminescence was employed to resolve the exact shape of the decay profile, and beam energy was varied from 0.8 to 4 keV. Beam pulses short compared to the activator decay times were generally used. Some saturation (pulse height) effects were seen, particularily at higher beam energies, but these will not be discussed here, and all data presented was taken below the threshold for such dependences. Decay data were directly compared to PL persistence profiles obtained on the same phosphors. Some dependence of the PL decays on excitation wavelength was observed. Some of these effects are due to site-to-site symmetry differences and are discussed elsewhere in some detail[5]. All of the PL data quoted here were obtained at an excitation wavelength of 225 nm.

An example of the observed CL decay is shown in figure 1. Here we have measured the 535nm CL emission from the $^5D_1$ state of $Eu^{3+}$ in Nichia[6] $Y_2O_3$ and compared it to PL excited with a 225nm laser pulse. The CL rises slightly after the end of the electron pulse due to energy transferred to the $^5D_1$ state from higher excited states[7], and the decay rate at short times depends significantly on beam energy. The PL displays a much more noticeable rise after the end of the pulse suggesting that the next higher ($^5D_2$) excited state has a longer lifetime when this phosphor is excited optically. A second example of CL decay data is shown in Figure 2, this time for decay of the 4 prominent CL lines corresponding to emission from the $^5D_3$ level of $Tb^{3+}$ in $Y_2SiO_5$. This material was grown by spray pyrolysis techniques at Superior Micropowders Inc[8] (SMP). In this data there is no evidence of a post-pulse-rise in either the CL or the PL, so the lifetime of the higher excited states of $Tb^{3+}$ are quite short on this time scale. However, the decay of the ($^5D_3$) CL always lies below the PL curve and is noticeably faster at short times for lower beam energies.

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We have measured decay profiles from yttria commercially available from Nichia[6], SPM yttria phosphors with 1 and 9% Eu, as well as Tb doped yttrium silicates from Nichia, and SPM $Y_2SiO_5$ having 0.2,1 and 10% Tb. The data obtained from all these materials is similar: CL decays are beam energy dependent and faster than those observed from 225 nm-excited PL. The beam energy effects are larger for higher excited states and more prominent at larger activator concentrations. Table 1 lists decay rate values observed for the upper excited state decays ($^5D_3$ for Tb and $^5D_1$ for Eu) for all six phosphors. Data from the decay of the lowest excited state ($^5D_4$ for Tb and $^5D_0$ for Eu) is qualitatively similar: the CL decays faster at short times, the amount of curvature on a log plot increases with increasing activator content, the long-time decay rates approach those seen for PL, and the beam energy dependence of the decay rates is noticeable, but typically smaller than for the upper excited states.

Steady state measurements of CL efficiency in these materials also demonstrate the influence of activator concentration on beam energy effects. This is illustrated in Figure 3 where data from both experimental phosphor systems are plotted. These measurements were done on powder patches at a current density of $\sim 2$ $\mu A/cm^2$, and data at beam energies from 0.75 to 3 keV was acquired rapidly to prevent any degradation effects. In the insert of this figure we show typical beam energy dependences of CL efficiency plotted versus $E_B$ on a log-log plot for the SMP $Y_2SiO_5$:Tb system. The main part of figure 3 is a plot of the **slopes** of these log (CL) versus log ($E_B$) plots at different activator concentrations. These slope values are a direct measure of the amount of beam energy dependence of the CL; zero slope at a particular $E_B$ value means that the CL does not vary with beam energy. These data demonstrate that the beam energy dependence of CL efficiency (evaluated here at 1 keV) is dropping noticeably for the Eu $^5D_0$ emission as the activator fraction is reduced; for the Tb $^5D_3$ and $^5D_4$ emission the drop is dramatic and a simple extrapolation suggests that it might vanish completely when x<0.0001.

It is generally assumed[2,3] that initial excitation of 4f – electron activator ions in the CL process begins in one or many of the upper excited states, either as a result of electron-hole recombination or direct impact excitation. We expect that all these excitation processes occur on a sub-nanosecond time scale after entrance of the primary (fast) electron. The excited activator ion then loses energy by a cascade process, emitting phonons and or photons as the ion returns to the ground state. Because the upper excited states of these 4f systems are closely spaced in energy, and because the probability for the emission of N phonons is proportional to exp(-N), phonon emission dominates until the lower energy, more widely spaced, excited levels become occupied. At this point the probability of radiative emission begins to dominate, and light characteristic of the lower level-to-ground state energy difference is emitted. In phosphors doped with $Tb^{3+}$, emission from $^5D_4$ to the $^7F_5$ ground state (at 543 nm) dominates at Tb levels above 1 at.%, but emission from the $^5D_3$ states (blue light) is seen as well[10]. In $Eu^{3+}$ doped phosphors red emission from the $^5D_0$ line (at 611 nm) dominates, but some light from higher energy transitions ($^5D_1$ (green) and $^5D_2$ (blue)) is also visible[11]. As the activator concentrations are raised in both these phosphor systems activator-activator interactions raise the probability of multiphonon emission from the upper excited states more than for the lower ones[10-12]. This shortens the decay time for the cascade process, raises the probability of non-radiative de-excitation to the ground state, and reduces the relative brightness of the higher energy spectral components. This spectral shift (as $N_a$ is increased) is more evident in $Tb^{3+}$-doped phosphors, but is also observable in quantitative spectral studies of $Eu^{3+}$ emission in $Y_2O_3$ and $Y_2O_2S$.

While the existence of activator-activator quenching is firmly established in these materials, and in fact determines the values of $N_a$ which are optimum for maximum PL and CL emission, the mechanisms for the coupling/loss process are not known with great precision. Exchange, magnetic dipole, and multipolar electrostatic interactions have been proposed on the basis of the observed functional form of the quenching[10-13] at high

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activator fractions, but the detailed quantum mechanical theory of these interactions and theoretical predictions for actual phonon emission rates appear to be lacking for specific phosphors. In addition, this mechanism is clearly host-dependent[11]. There is also the general issue of whether activator-activator coupling leads to non-radiative loss in a defect free lattice, or whether the activator-to-activator transfer of energy primarily facilitates migration of this energy to non-radiative centers (defects or impurities)[8,10-13]. These issues are coming under increased scrutiny because of their impact on rare-earth doped semiconductor lasers and fiber optic amplifiers[14].

At low electron beam energies (0.1 – 4 keV) the rate of energy deposition along the primary electron track increases as $\sim 1/\sqrt{E}$, reaching values as high as 7-10 eV/Å for low density materials (C for example)[15], and considerably higher for common phosphor hosts. Under these conditions it would appear likely that the probability for finding *excited* activators that are spatially dense is enhanced. *We propose that the interaction of these excited states could create enhanced non-radiative losses over and above those expected from the standard excited state-ground state quenching process.* Note that because the intense excitation regions present around primary electron tracks created by multiple incident electrons rarely overlap, the existence of this mechanism does not necessarily imply any beam current dependence of this process at beam current densities below a few $\mu A/cm^2$.

While the observed beam energy dependence of the decay rates is generally less than the actual changes in cw CL efficiency, the multiple step nature of the cascade process must be taken into account when assessing the importance of these small rate differences. For example, if activator ions de-excite through a series of N excited states to the lowest excited state, and at each step lose a fraction of energy f via direct, non-radiative transitions to the ground state (due, for example, to excited state-excited state interactions), then the total fraction of energy left for radiant emission will be $\sim (1-f)^N$. If, for example, f is 0 for 4 keV and 0.2 for 0.8 keV (in Table 1, decay rates are ~20%

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faster at 0.8 keV than at 4 keV), the ratio of remaining energy available for luminescence at 4 keV over that at 0.8 keV is $(1-.2)^{-N}$. If N is 5, $(1-.2)^{-N}$ is 0.33, which is a typical ratio of efficiencies observed at these two beam energies for the materials (for $0.01 \leq x \leq .05$) in table I. So the multi-step nature of the cascade process tends to magnify the importance of any decay rate changes observed with beam energy.

Alternative explanations of the decay rate data in Table must be examined. These might include enhanced defect or activator densities near phosphor particle surfaces, regions which are preferentially excited at low beam energies. However it is important to note that PL (488nm excitation) decay studies[5] of $^5D_4$ emission in the SMP Tb doped silicates yield decay rates that are constant within 1% as the Tb content is varied from 1-10%. On the other hand, CL $^5D_4$ emission data on both SMP and Nichia powders (not shown in Table 1) display initial decay rates which typically increase by 12-40 % as the beam energy drops from 4 to 0.8 keV. This indicates that near-surface activator density enhancements cannot be the cause of the observed CL decay behavior in this system. In assessing the possible importance of enhanced near-surface defects, we emphasize that synthesis of the commercial Nichia material and the SMP phosphors is quite different (the latter powders have not been subjected to ball milling and extensive high temperature anneals); however, the main features of the CL decay curves are quite similar. This suggests that the beam energy dependent decays might be an intrinsic attribute of the CL process at low electron energies.

Finally, as an alternative to the excited state-excited state quenching hypothesis, we note that enhanced energy transfer rates between activators at higher rare earth concentrations will favor migration of energy to phosphor particle surfaces where it could be dissipated non-radiatively. When the initial excitation profile is closer to the surface (at low electron beam energies), CL efficiencies would be more strongly reduced. However, for electron beam energies above ~2 keV, intra-activator transfer would have to proceed over distances of several hundred angstroms if more than a few percent of the

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deposited energy is to reach the phosphor surface in this manner. Efficient transfer over such distances seems unlikely, so this mechanism seems somewhat improbable.

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Table 1.  CL decay times for emission from $^5D_4$ levels of $Tb^{3+}$ and $^5D_1$ levels of $Eu^{3+}$ in $Y_2SiO_5$:Tb and $Y_2O_3$:Eu.   The values labeled $\tau_s$ are the decay times (1/rate) measured at 4 keV after the end of the pulse; those labeled $\tau_l$ are those obtained from the CL decay curves after the luminescence has declined by factor of ~30.   Values in parentheses were measured at a beam energy of 0.8 keV.  Comparable decay times measured during laser-excited photoluminescence from these states are labeled $\tau_{ps}$ (immediately after excitation) and $\tau_{pl}$ (measured after a factor of ~30 decay).

| Phosphor | $\tau_s$ ($\mu$sec) | $\tau_l$ ($\mu$sec) | $\tau_{ps}$($\mu$sec) | $\tau_{pl}$($\mu$sec) |
|---|---|---|---|---|
| SMP $Y_2O_3$:1% Eu | 136(117) | 129(n/a) | | |
| Nichia $Y_2O_3$:5% Eu | 71(65) | 98(91) | 72 | 79 |
| SMP $Y_2O_3$:9% Eu | 26.3(18.5) | 83.6(n/a) | | |
| SMP $Y_2SiO_5$:0.2% Tb | 748(649) | 1290(1335) | 798 | 1339 |
| SMP $Y_2SiO_5$:1% Tb | 202(167) | 849(934) | 251 | 824 |
| Nichia $Y_2SiO_5$: Tb | 16.6(14.6) | 117(n/a) | | |
| SMP $Y_2SiO_5$:10% Eu | 5.4(3.4) | 29.1(n/a) | | |

Figure captions

Figure 1. A log plot of the CL at 535nm measured after a 10 μsec pulse of electrons incident on a screen of Nichia $Y_2O_3$ doped with ~4.6% Eu. The data does not fit a single exponential decay process, and the initial decay rates are a noticable function of beam energy. The 225 nm-laser-excited PL at the same emission wavelength is shown as filled circles, normalized to the CL value at the end of the electron pulse

Figure 2. A log plot of the CL from 360-470nm measured after a 10 μsec pulse of electrons incident on a screen of $Y_2SiO_5$:1%Tb. The initial decay rates of the light emitted from the $^5D_3$ level are a noticable function of beam energy. The 225 nm-laser-excited PL emitted at 417 nm is shown as filled circles, normalized to the CL value at the end of the electron pulse.

Figure 3 Insert- a log-log plot of the CL efficiency at 543 nm ($^5D_4$ emission) versus beam energy for two samples of SMP $Y_2SiO_5$ [circles, 10%Tb, squares 0.2% Tb (data multiplied by 0.56)]. These data are plotted over the beam energy range from 0.75 to 3 keV. The power law slope efficiency versus beam energy log-log plots like these (evaluated at 1 keV) is shown as a function of activator concentration in the main part of this figure for samples of $Y_2SiO_5$:Tb and $Y_2O_3$:Eu. The solid circles are for emission from the (lowest excited) $^5D_0$ state of Eu, the solid triangles are for emission from the (lowest excited) $^5D_4$ state of Tb, and the open squares are for emission from $^5D_3$ state of

Tb. The beam energy dependence increases with activator fraction in both materials, but more quickly in the $Y_2SiO_5$:Tb system.
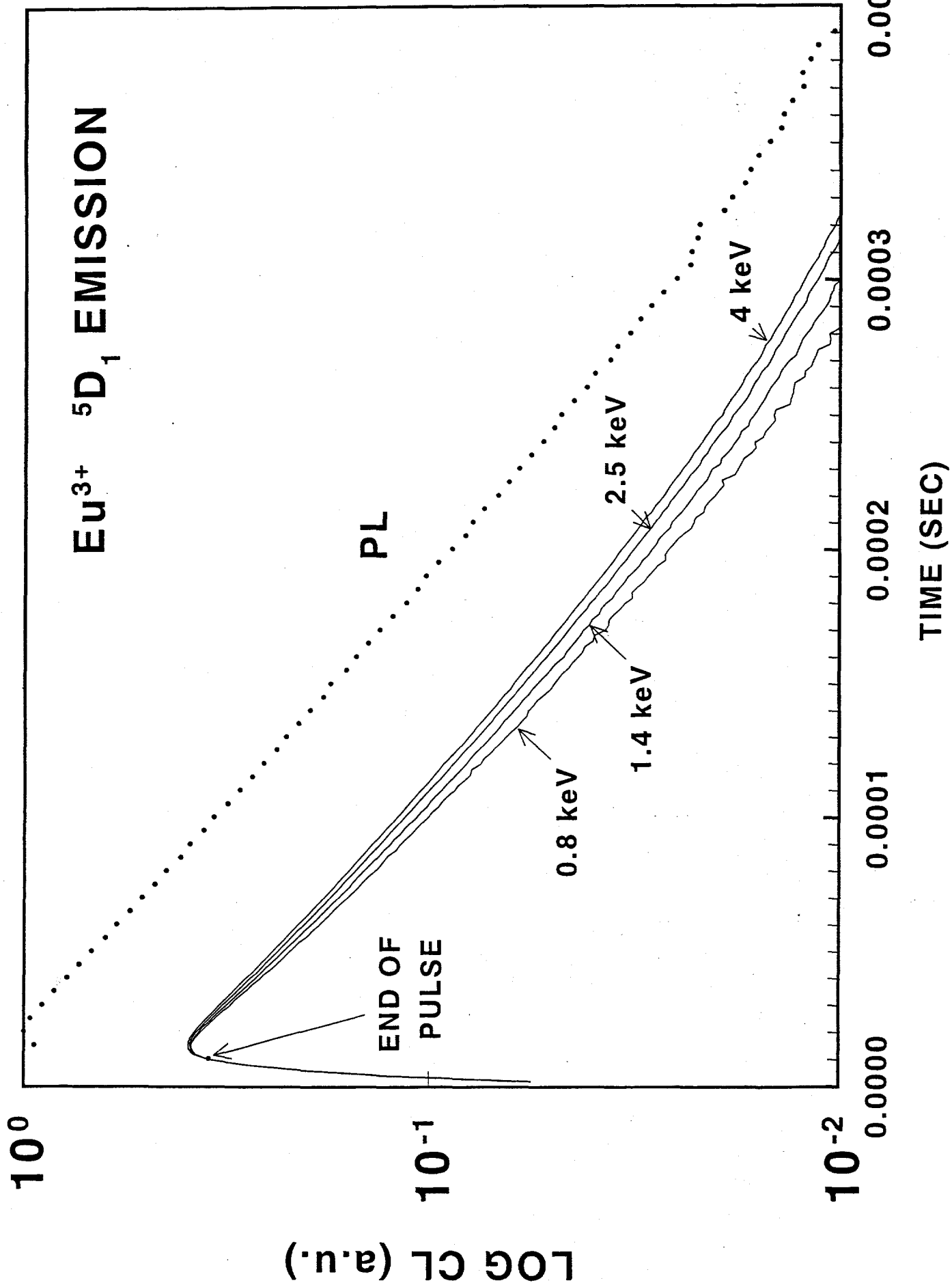
Eu$^{3+}$  $^5D_1$ EMISSION
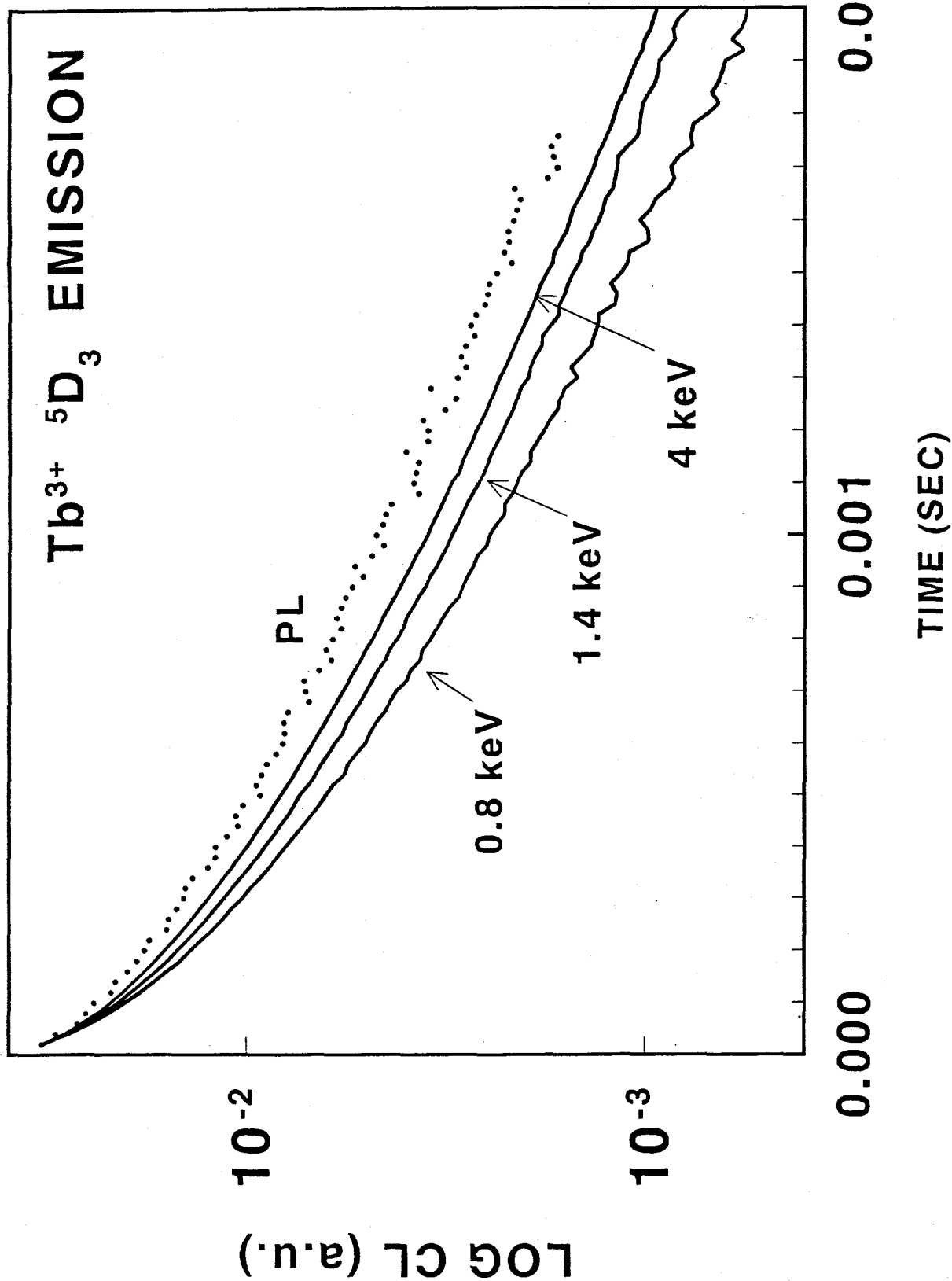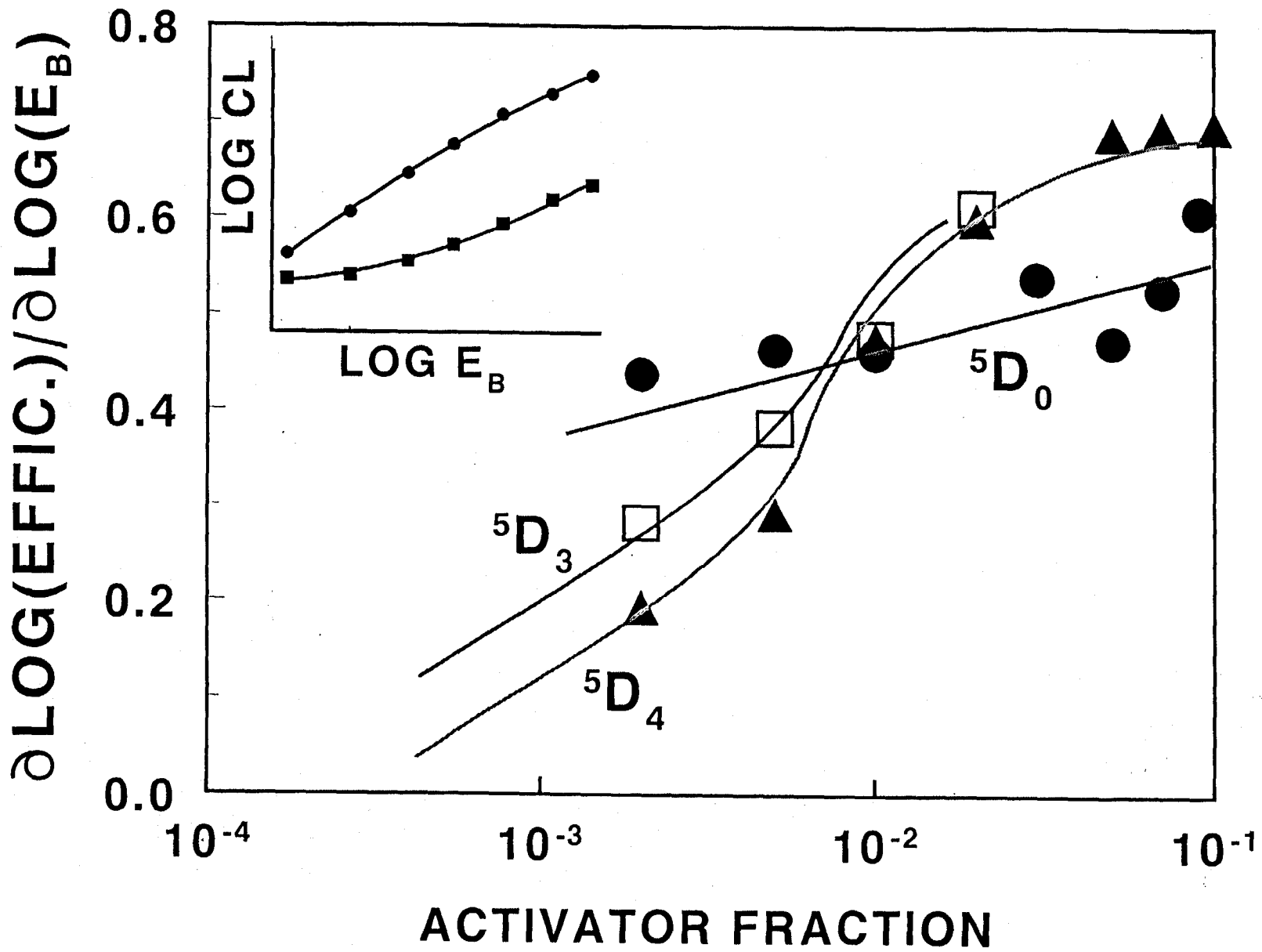
PL

4 keV

2.5 keV

1.4 keV

0.8 keV

END OF
PULSE

LOG CL (a.u.)

TIME (SEC)

$10^0$  $10^{-1}$  $10^{-2}$

0.0000  0.0001  0.0002  0.0003  0.0004

FIG. 1

npyf1

Tb$^{3+}$ $^5$D$_3$ EMISSION

PL

0.8 keV

1.4 keV

4 keV

LOG CL (a.u.)

$10^{-2}$

$10^{-3}$

0.000

0.001

0.002

TIME (SEC)

Y1TBF1

FIG. 2

Fig. 3

eutbf3