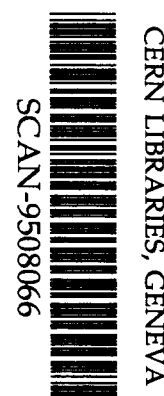




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Luminescence quenching studies in fast scintillator materials by ns time resolved VUV-spectroscopy

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ABSTRACT

The quenching mechanisms for fast luminescence in CeF_3 and $\text{CeF}_3 - \text{LaF}_3$ crystals have been studied by means of time-resolved VUV-spectroscopy using synchrotron radiation. The luminescence decay of these crystals reveals at least three mechanisms of quenching: the first one, conventional for VUV region, where the radiation penetration depth is very small ~ 10 nm, results from surface losses; the second one is due to the energy transfer to defect centres in the bulk of the crystal (very pronounced in $\text{CeF}_3 - \text{LaF}_3$) and the third one, the least studied, is attributed to the interaction of closely spaced electron excitations (secondary electron excitation quenching). Temperature and energy dependencies of decay kinetics clearly indicate that this new quenching mechanism comes into play above the energy corresponding to the threshold of impact excitation of Ce^{3+} - ions by hot photoelectrons. The magnitude of secondary electron excitation quenching decreases with the mobility of the electron excitations.

I. INTRODUCTION

For the successful use and manufacture of fast scintillator materials which have wide practical applications both in high energy physics and medicine [1,2] the understanding of fundamental processes responsible for quenching of the luminescence is crucially important. In the wide band gap scintillator crystals, CeF_3 and BaF_2 , an unusual type of quenching of prompt intrinsic luminescence under moderate intensity VUV excitation has been observed recently [3,4]. It is assumed that the effect is associated with a non-radiative energy transfer between the VUV excited luminescence centre (the $(\text{Ce}^{3+})^*$ or $5p\text{Ba}^{3+}$ core hole) and the nearest electron excitations created by the same absorption process [5]. This mechanism was advanced as an explanation of quenching seen in the initial stage of luminescence decay after X-ray excitation in some nanosecond scintillators [6,7]. The closely spaced interacting electron excitations are formed by inelastic scattering of primary photoelectrons and Auger relaxation of core photoholes created by the absorption of the VUV photon. Since the mean free path of the photoelectron excited by the VUV photon with energy $E > 2E_g$ in respect of electron-electron inelastic scattering has a value of about 0.5 nm [8], we expect that even after the process of the thermalisation the distance between secondary electron excitations could be comparable with the radius R_0 of dipole-dipole energy transfer with the rate $W \sim \tau^{-1} (R_0/R)^6$ [9], where τ is the lifetime of the electron excitations. For instance, in case of resonance transfer from the $5p\text{Ba}^{3+}$ core-hole to the Ce^{3+} ion in barium fluoride, R_0 is about 1.2 nm [10].

This effect, which visualises the fundamental process of electron-electron inelastic scattering in crystalline materials, is believed to be important for many fast luminescent crystals and must be studied further. As the minimum threshold for electron-electron scattering is about $2E_g$ the use of VUV excitation allows to follow how this mechanism switches on. In this region the absorption coefficient is very high, i.e. the radiation penetration depth is very small (less than 10 nm) and near surface luminescence quenching should be taken into account [11].

The aim of this research is to extend our investigations into the effects of luminescence quenching in pure CeF_3 and mixed $\text{CeF}_3 - \text{LaF}_3(10\%)$ crystals, paying especial attention to non-radiative energy transfer between the luminescent centre Ce^{3+} and the nearest secondary electron excitations.

II. EXPERIMENTAL PROCEDURE

CeF₃ - LaF₃ crystals with a concentration of 10% LaF₃ were grown by the Stockbarger-Bridgeman method in a fluorine atmosphere. Crystals were cleaved just prior to their installation into the cryostat. The CeF₃ sample was a high purity powder with a total impurity concentration of less than 20 ppm.

Synchrotron radiation from the SRS (Daresbury Laboratory) was used as a light source. The excitation and emission spectra were measured in multibunch operation while luminescence decay curves were derived in singlebunch mode of the SRS on station 3.1, using a 1 m Seya-Namioka monochromator covering the VUV photon range 5 - 35 eV [12]. The luminescence was observed via interference filters and a visible/UV monochromator (SPEX Minimate) with a resolution of 5 nm. Low temperature measurements were performed using an UHV continuous flow helium cryostat (Oxford instruments) with temperature controller (model ITC4) . The residual pressure in the sample chamber during collection of experimental data was $2 \cdot 10^{-7}$ Pa.

Luminescence decay time studies were made using the single photon coincidence method [13]. Decay curves were reasonably well fitted by a sum of three exponentials using the computer code FLUOR [14]. The derived decay times fall into three range: $\tau_1 \sim 2\text{-}4$ ns for the shortest one; $\tau_2 \sim 12\text{-}20$ ns and $\tau_3 \sim 40\text{-}60$ ns. The large range of parameters is caused by a complicated non-exponential decay law due to the combination of different quenching mechanisms. The emission decay of 'perturbed' Ce³⁺ was characterised by rise time in agreement with the model of luminescence in CeF₃ like system [3, 15 - 22].

III. EXPERIMENTAL RESULTS AND DISCUSSION

A. Emission and excitation spectra

Figure 1 presents the luminescence spectrum of CeF₃-LaF₃ at 300 K and 20 K excited at 8.4 eV photon. We can see four main features at wavelengths 290, 310, 325, and 390 nm. The first two bands correspond to emission from the 'normal' (unperturbed) Ce³⁺ in the cation position [3,15,18,23] while the later two are associated with Ce³⁺ perturbed by some impurity or intrinsic defects, e.g. O²⁻ or (and) an anion vacancy in its first co-ordination sphere [18,20] .The same situation has been observed in pure cerium fluoride and CeF₃ activated by the divalent cations Ca²⁺, Cd²⁺, Ba²⁺ where the broad emission band of 'perturbed' Ce³⁺ luminescence was in the spectral region 320-380 nm [3,19,20]. Luminescence studies of pure CeF₃ powder have not shown the perturbed Ce³⁺ emission.

Figure 2 shows the excitation spectrum of the normal and perturbed emission bands at 300 K. The spectra are very similar to each other and that of pure CeF_3 measured previously [3,24]. The structure in the region 5 - 7 eV corresponds to the excitation $4f \rightarrow 5d$ while the wide band at 8.4 eV can be attributable to the $4f \rightarrow 6s$ transitions of Ce^{3+} or charge transfer of $2p\text{F}^- \rightarrow 6s\text{Ce}^{3+}$ in CeF_3 [18,25]. In the energy region 10 - 35 eV we observed two wide bands, at 10 - 15 eV and 20 - 27 eV and an increase of the luminescence efficiency at energies above 30 eV. The latter region corresponds to the electronic transitions with strong absorption from the $2p\text{F}^-$ valence band and 5p levels of lanthanides to conduction band [26].

B. Decay curves

Temperature dependence

Fig.3 presents the decay curves for normal emission Ce^{3+} for both compounds and perturbed Ce^{3+} luminescence in $\text{CeF}_3 - \text{LaF}_3$ following excitation in the region of the $4f \rightarrow 5d, 6s$ transitions. Fig.4 demonstrates the temperature dependences in the range 20 - 300 K for decay curves of the normal Ce^{3+} emission in $\text{CeF}_3 - \text{LaF}_3$ crystals and their asymptotic approach to the decay curve of pure CeF_3 at 20 K (top curve Fig.4.). The deviation from one exponential decay law for $\text{CeF}_3 - \text{LaF}_3$ is supposed to be mainly associated with non-radiative resonance energy transfer from normal $(\text{Ce}^{3+})^*$ to perturbed Ce^{3+} [18,20,21]. For pure CeF_3 the time decay slightly decreases with temperature, without any significant changes.

Excitation energy dependence

In the excitation region, corresponding to the Ce^{3+} absorption from 5 to 10 eV, the radiation penetration depth is rather high and the surface losses are small. However, in the region of transitions involving the fluorine states ($E > 10$ eV [26]) the surface quenching is expected to be higher. Both these cases are illustrated in fig.5 for $\text{CeF}_3 - \text{LaF}_3$ at low temperature, when the non-radiative energy transfer between normal and perturbed Ce^{3+} could be ignored. It is interesting that at lower energy 12.4 eV (Fig.5.) the shortening of the decay is not so strong in comparison with that at 20.7 eV, despite a decrease in the absorption coefficient from $1.6 \cdot 10^6$ to $1.2 \cdot 10^6 \text{ cm}^{-1}$. The changes in absorption coefficient were estimated by the Kramers-Kronig analysis of the reflectivity spectrum for s-polarised light of crystal CeF_3 measured in [26]. Therefore there must be an additional quenching mechanism if neither surface losses nor resonance energy transfer to perturbed Ce^{3+} - centres could decrease the decay time so strongly. We suggest that it is the non-radiative energy transfer between the normal excited Ce^{3+} and the nearest secondary electron excitation that is responsible for generating the strong luminescence quenching. The closely spaced secondary electron excitations are created above the energy region from 15

to 17 eV for CeF₃ as a result of inelastic scattering of the fast electron on Ce³⁺ ions (i.e. impact excitation of Ce³⁺ ions [24, 27]).

The assumption that the dominant mechanism of quenching changes between 12.4 and 20.4 eV is confirmed by Fig.6, where the temperature dependence of decay curves in CeF₃ with excitation above and below the threshold energy for impact excitation of Ce³⁺ ions, is presented. The effect of temperature on the decay curves is reversed in these two cases. For an excitation energy at 12.4 eV (two upper curves in Fig.6), when the surface losses are assumed to be dominant, the luminescence quenching is greater at room temperature than at 20 K. Two mechanisms of the surface quenching are postulated [11]: namely, resonance and (or) diffusion energy transfer from electron excitations to the quenching centres, the concentration of which is much larger near to the surface than in the volume of a crystal. Thus we can conclude that the faster decay of the luminescence with temperature, at an excitation of 12.4 eV, is associated with the increasing diffusion mobility of electron excitations. The reverse effect with temperature is observed at an excitation energy of 20.7 eV when the secondary electron excitation at a distance $\sim R_0$ from (Ce³⁺)^{*} can be created such that secondary electron excitation quenching can take place. In the latter case the rise of electron excitation mobility with temperature will increase the mean distance R between (Ce³⁺)^{*} and electron excitation created in the same absorption process which reduces the probability of secondary electron excitation quenching.

IV. CONCLUSIONS

The quenching due to the interaction with geminate secondary electron excitations has been identified in pure CeF₃ and CeF₃-LaF₃ crystals. In these fast scintillators the Ce³⁺ luminescence is quenched by the nearest electronic excitation (excited Ce³⁺, electrons or hole etc.) created by the same absorption process, as a result of inelastic scattering of the hot photoelectron (or Auger decay of core hole). It has been shown that secondary electron excitation quenching effect takes place once the excitation energy is sufficient for the creation of secondary electron excitations and obviously starts with the threshold of the electron multiplication in the scintillator. The magnitude of secondary electron excitation quenching seems to decrease with the mobility of the electronic excitations.

The surface losses are traditionally assumed to be the main mechanism of luminescence quenching with VUV excitation but this work demonstrates that such is not always the case. For CeF₃ and CeF₃ - LaF₃ at an excitation energy of 20.7 eV,

secondary electron excitation quenching effect is more significant than near surface losses.

The understanding of this quenching effect is extremely important for practical scintillator applications particularly those where the scintillator detectors are operated in the VUV and soft X-ray regions where the mean free path of photo and secondary electron excitations is very small.

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FIGURE CAPTIONS

Fig.1 The emission spectrum of $\text{CeF}_3\text{-LaF}_3(10\%)$ (a) at 300 and (b) 20 K.
Excitation energy $E_{\text{ex}} = 8.4$ eV.

Fig.2 The luminescence excitation spectra of $\text{CeF}_3 - \text{LaF}_3(10\%)$ for (a) normal Ce^{3+} (290 nm) and (b) perturbed Ce^{3+} (390 nm) at 300 K.

Fig.3 Decay curves at 300 K and $E_{\text{ex}} = 8.4\text{eV}$.
a) normal Ce^{3+} emission of $\text{CeF}_3 - \text{LaF}_3 (10\%)$;
b) perturbed Ce^{3+} emission of $\text{CeF}_3 - \text{LaF}_3 (10\%)$;
c) normal Ce^{3+} emission of pure CeF_3 .

Fig.4 Decay curves for normal Ce^{3+} emission for $E_{\text{ex}} = 8.4$ eV in $\text{CeF}_3 - \text{LaF}_3(10\%)$ at $T = 300, 200, 150, 100$ and 50 K. The lifetime increases steadily from 300 K (the lowest) to 50 K (upper) curve (—). The top curve is CeF_3 at $T = 20\text{K}$ (·····).

Fig.5 Decay curves of normal Ce^{3+} emission from $\text{CeF}_3 - \text{LaF}_3 (10\%)$ at 20 K.
 $E_{\text{ex}} = 8.4$ upper, 12.4 centre and 20.7 eV lower curve respectively.

Fig.6 Decay curves for normal Ce^{3+} emission from CeF_3 at $E_{\text{ex}} = 12.4$ eV (the upper two curves) and 20.7 eV (the lower two curves).
 $T = 300$ K (—), 20 K (·····).

Fig. 1.

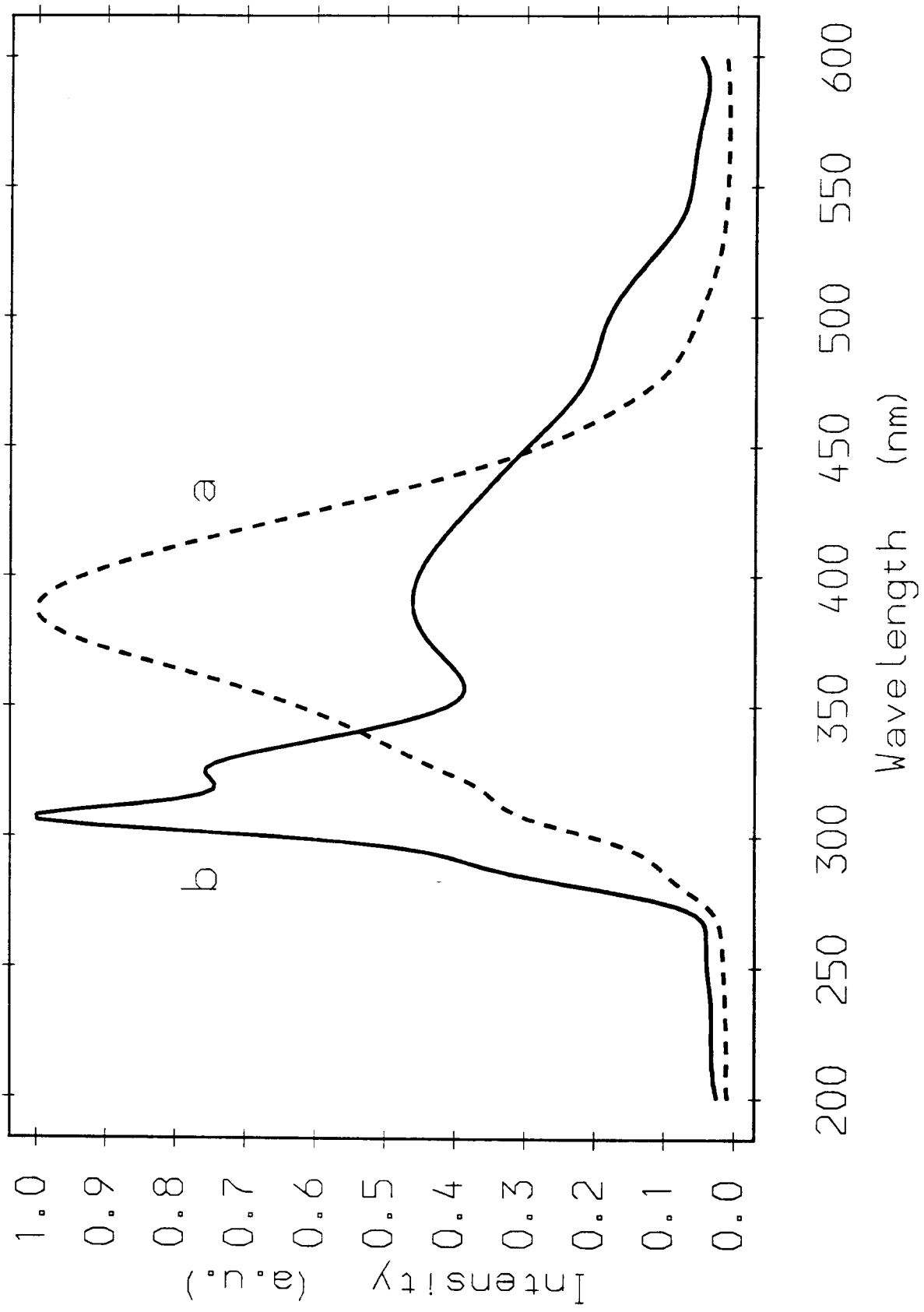


Fig.2.

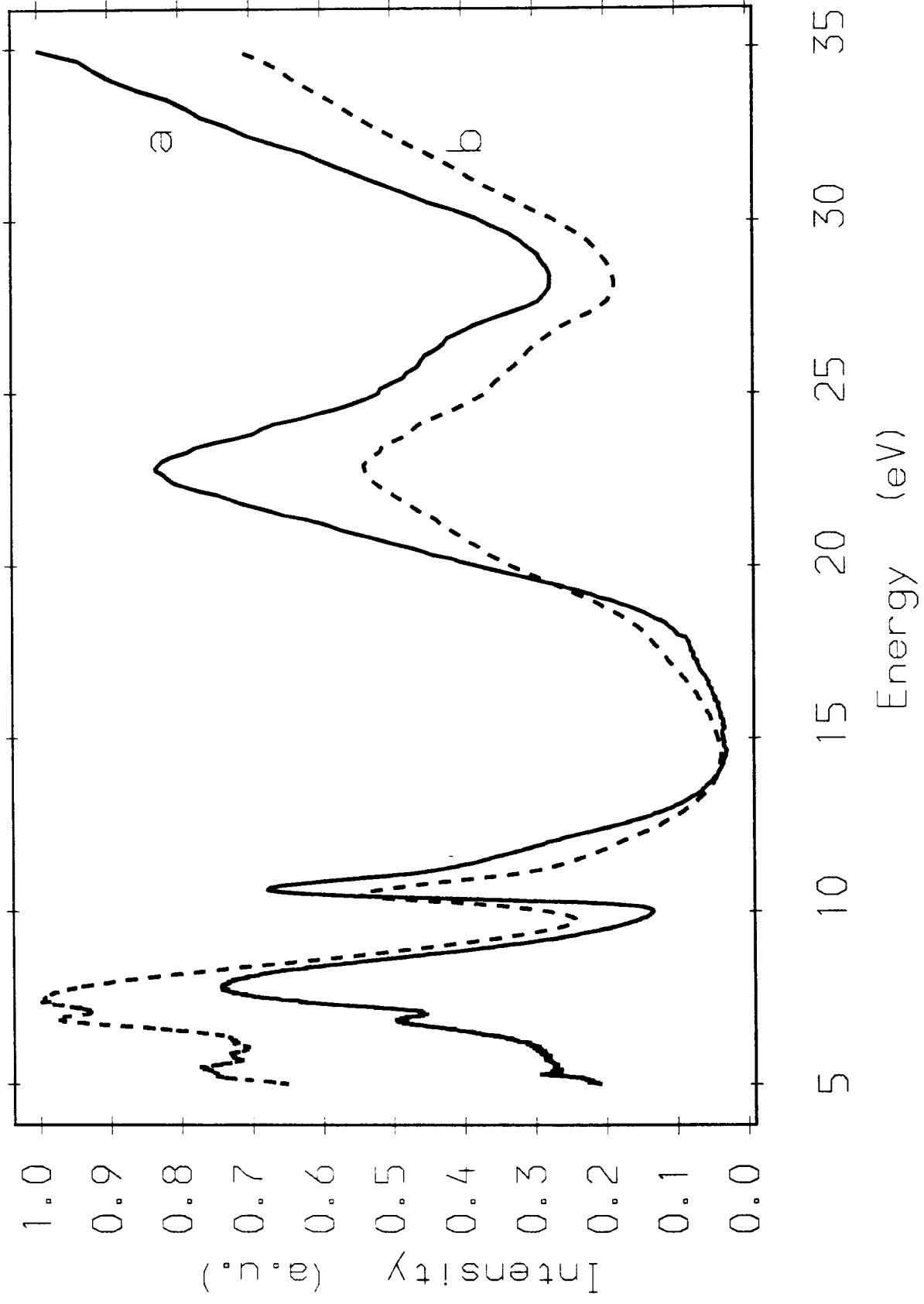


Fig. 3.

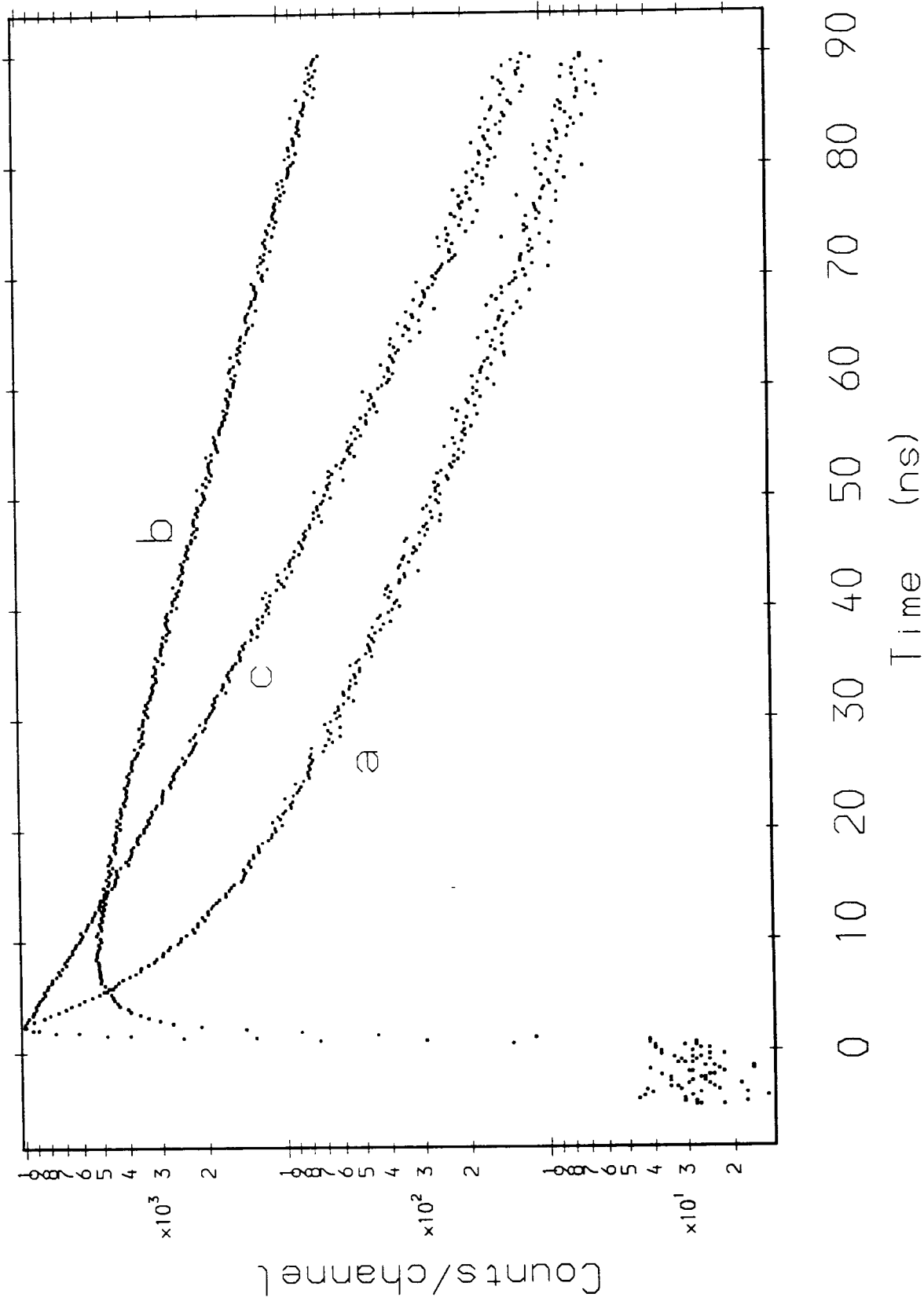


Fig. 4.

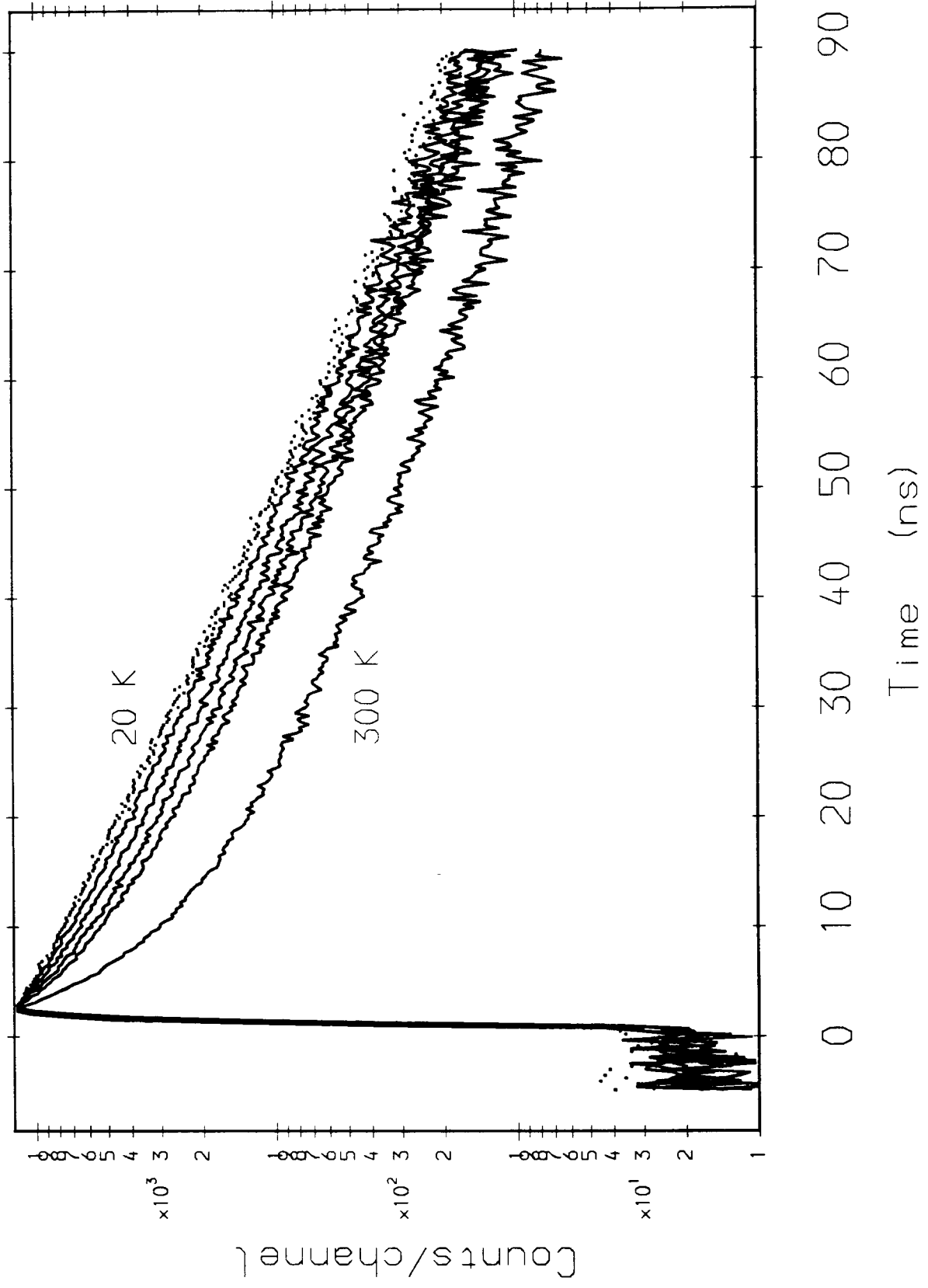


Fig.5.

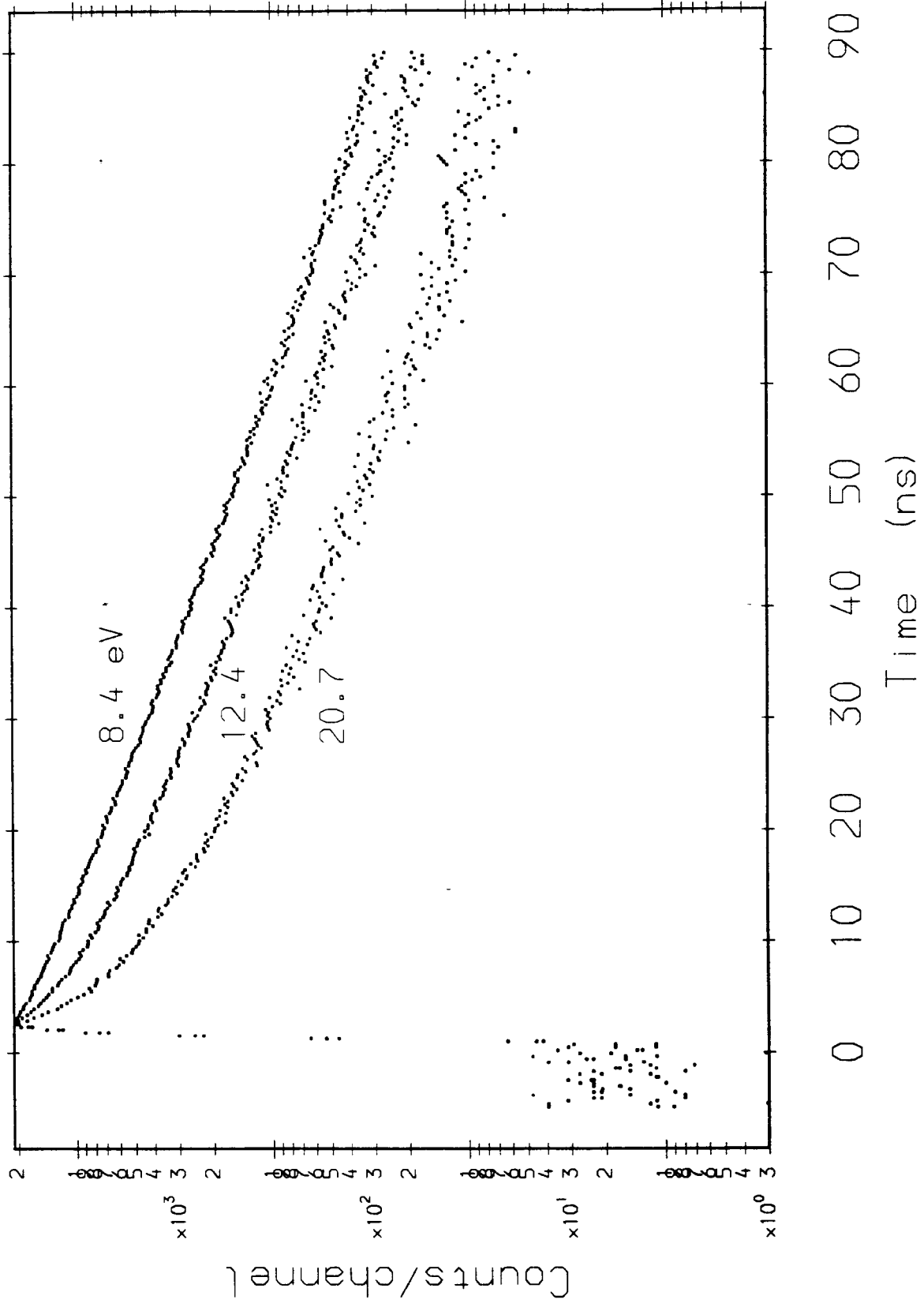


Fig. 6.

