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by

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Decay times of the intrinsic luminescence band (1750 Å) of solid Xe *)

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Thin films of solid Xenon have been excited by a pulsed electron beam with electron energies of 300 eV and pulse lengths down to 5 nsec at low current. For the main luminescence band of solid Xenon ($\lambda \approx$ 1750 Å) two decay times have been observed. The short decay time $\tau_1 = 3 \pm 1$ nsec is independent of temperature between 4 K and 30 K, whereas the long decay time τ_2 decreases from $\tau_2 = 900 \pm 50$ nsec at 4 K to $\tau_2 = 150 \pm 50$ nsec at 30 K.

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In view of the development of the Xenon gas laser decay times of the fluorescence of gaseous Xenon have been measured for a large range of pressures and at different temperatures [1]. In high density Xenon the radiative decay of vibrationally relaxed Xe_2^* molecules is observed (2 nd continuum). This fluorescence band contains two decay components: a fast one assigned to $^1\Sigma_u^+ \rightarrow {}^1\Sigma_g^+$ and a slow one assigned to $^3\Sigma_u^+ \rightarrow {}^1\Sigma_g^+$. In testing the use of solid Xe for an ablation laser a decay time of 4 ± 2 nsec at 70 K has been observed by high current electron excitation [2] but no systematic investigation has been reported. In this paper decay times for solid Xenon in the temperature range of 4 K up to 30 K are presented. They are compared with the results for high density Xenon gas and discussed in terms of a model proposed for alkalihalides. From the close correspondence of the emission bands a strong correlation between the results for high density gas and the solid is expected and in fact also in the solid two decay times are observed, where the short one τ_1 agrees quite well with the value of the gas. But the observed temperature dependences of the long decay time yields for solid Xenon either a much smaller splitting between the lowest $^3\Sigma_u^+$ and $^1\Sigma_u^+$ states or the assignment has to be different in the solid.

Thin films of solid Xe have been deposited onto a Helium flow cryostat under UHV conditions at a background pressure smaller than 10^{-9} torr. Xe gas from L'Air Liquide with a purity of better than 99.99 % has been used. The thickness of the samples varied between 1000 Å and 10 µ. The samples have been excited by a pulsed electron beam of 300 eV with pulse lengths between 5 nsec and 100 nsec and rise and fall times shorter than 1 nsec. The beam current has been kept low(5×10^{-6} A)during pulse duration; thus given the rate constants for collisional mixing in Xe gas [2] our measured decay times should not depend on electron concentration. The luminescence light has been dispersed by a Seya Namioka monochromator, where the electron focus at the sample served as an entrance slit [3]. A Valvo 56 DUVP photomultiplier with quartz window has been used to avoid a converter material.

The right insert in fig.1 shows three emission spectra of solid Xe at 5 K with a resolution of ≈ 100 Å. The curves have been corrected for the detector characteristics. Two bands are observed, the well kown Xe emission band centered at 1750 Å and a comparable weak emission around 3000 Å. Curve 1 shows a measurement immediately after deposition of the film, curve 2 was measured 30 minutes later, for curve 3 additional Xe was deposited and a curve 4 would again correspond to curve 2. Evidently both emissions are quenched by contamination of the sample but the 1750 Å emission decreases stronger. Also in thin films the intensity ratio of the 3000 Å band to the 1750 Å band is enhanced. At the present state an assignment of the 3000 Å band to impurity or intrinsic emission is not evident[4].
For the decay time measurements the single photon counting technique has been applied [5]. The time delay between a luminescence event and its excitation pulse has been monitored by a time to pulse hight converter at a yield of one event for more than 100 excitation pulses. These single time measurements have been collected in a multichannel analyzer. The time resolution of the electronics is better than 0.5 nsec. The pulse lengths of the multiplier are 4 nsec and the jitter is less than 0.5 nsec. Thus including the fall time of the excitation pulse a resolution of at least 1 nsec has been achieved. Fig.1 shows a typical decay curve for the 1750 Å band of solid Xe at 30 K. Evidently two components with very different decay constants contribute to the emission band. Therefore the experimental curves have been fitted with two exponential decay times τ_1 and τ_2 according to equ.1 where A_1 and A_2 are the intensities of the components and t_o is the width of the exciting electron square pulse.

1)
$$I(t) = \begin{cases} A_1(1-\exp(-t/\tau_1)) + A_2(1-\exp(-t/\tau_2)) & 0 \le t \le t_o \\ A_1(\exp(t_o/\tau_1)-1)\exp(-t/\tau_1) + A_2(\exp(t_o/\tau_2)-1)\exp(-t/\tau_2) & t_o < t \end{cases}$$

The decay times and the intensity ratio A_1/A_2 are listed in table 1 in the temperature range 4 K to 30 K. The temperatures have been measured at the cryostat therefore a shift up to 3 degrees to higher temperatures at the sample is possible. The decay times represent mean values of several measurements with the scattering indicated by the error bars. A systematic decrease with time of the decay times after deposition has been observed. Obviously this decrease is correlated with quenching due to contamination (see insert fig.1). Also the decay time at 2600 Å has been determined (see table 1).

According to our observation the 1750 Å luminescence band of solid Xe consists of two components, one with a decay time of 3 nsec which is independent on temperature from 4 K to 30 K and one with a long decay time. The long decay time decreases from 900 nsec at 4 K to 150 nsec at 30 K. This temperature dependence is not caused by thermal quenching to nonradiative decay channels because within this temperature range the total intensity of the 1750 Å band does not change within our accuracy of 10 %. Also the spectral distribution of the emission does not show a marked change. Therefore the temperature dependence is attributed to a phonon activated depopulation of the states with a long decay constant to those with a fastdecay constant. $\tau_1(T)$ and $\tau_2(T)$ are fitted with equ.2 on the basis of the scheme in fig.2 with the two excited states A, B and the ground state C. $1/\tau_{oa}$ and $1/\tau_{ob}$ are the phonon activation rates and τ_{ra} and τ_{rb} the radiative decay times for the two states. This scheme has been used by Fischbach et al for the emission from triplet states in alkali halides [6].

2)
$$1/\tau_{1,2} = 1/2\,(\bar{n}/\tau_{oa} + 1/\tau_{ra} + (\bar{n}+1)/\tau_{ob} + 1/\tau_{rb}) \pm$$
$$\pm\left[1/4\,(\bar{n}/\tau_{oa} + 1/\tau_{ra} + (\bar{n}+1)/\tau_{ob} + 1/\tau_{rb})^2 - ((\bar{n}+1)/\tau_{ob}\cdot\tau_{ra} + \bar{n}/\tau_{oa}\tau_{rb} + 1/\tau_{rb}\tau_{ra})\right]^{1/2}$$

$$\bar{n} = (\exp(E_{ba}/kT) - 1)^{-1}$$

The left insert in fig.1 shows the result of the fit (solid line) together with the experimental points (see also table 1, 2). The limited temperature range together with the error bars yields great uncertainities in the values of τ_{oa} and τ_{ob}, whereas τ_{ra}, τ_{rb} and E_{ab} are insensitive to the fit procedure.

It is now generally agreed that the second continuum of high density Xenon gas (1720 Å) consists of two components: the emission from the $^3\Sigma_u^+$ (1_u) and $^1\Sigma_u^+$ (0_u^+) states with decay times of ≈ 100 nsec and 4 nsec respectively[1]. The short decay time corresponds to the allowed transition from 0_u^+ to the ground state and the decay constant of the 1_u state is mainly determined by the mixing of 1_u with Π_u states by spin-orbit interaction[1]. The splitting of the 0_u^+ state and the center of $^3\Sigma_u^+$ substates 1_u and 0_u^- was estimated by Mulliken to 0.24 eV[7,8] and calculated by Lorents et al to 0.2 eV[1].

Keto et al. determined from the temperature dependence between 200 K and 300 K a splitting of 0.04 - 0.08 eV[1].

The position and the line shape of the second continuum in solid and also liquid rare gases is quite similar to that of the gaseous phase[9] and therefore it was deduced that in all three phases the emission is due to the decay of excited rare gas eximers R_2^* and that these centers are only weakly disturbed by the surrounding atoms. Our observed decay times in solid Xenon seem to confirm this close correspondence of the emission centers. The fast decay times are nearly equal and the longer decay time of 900 nsec in solid Xenon has been measured at lower temperatures. But in the solid phase the splitting E_{ab} of 5 meV (see table 2) of the states involved is at least one order of magnitude smaller than the measured and calculated values for the gaseous phase.

The observed splitting fits much better to the splitting of the 0_u^- and 1_u substates of $^3\Sigma_u^+$ which was estimated by Lorents at al[1] to be smaller than 10 meV for Xe_2^*.

Molchanov[10] has pointed out that in the solid phase the symmetry for the Xe_2^* center is reduced from $D_{\infty h}$ to D_{2h} and the degeneracy of the states is lifted. Thus 1_u corresponds to Γ_2' and Γ_4', 0_u^- to Γ_1' and 0_u^+ to Γ_3'. A very similar electronic structure is attributed to the self-trapped excitons in alkali halides[6]. The splitting of Γ_2' and Γ_4' should be very small, whereas the splitting between Γ_1' and the center of Γ_2' and Γ_4' is of the order of meV in alkali halides and corresponds to the $0_u^- - 1_u$ splitting of less than 10 meV as discussed by Lorents et al. If we attribute the observed 5 meV energy barrier to this splitting the decay time of 900 nsec belongs to the Γ_1' and the decay time of 3 nsec to the Γ_2' and Γ_4' states. The optical transition of Γ_1' to the ground state is strictly forbidden but one could argue that the observed decay time is influenced by quenching. Transitions from Γ_2' and Γ_4' are symmetry allowed but a decay time of 3 nsec would be very short compared with alkali halides where it is of the order of µsec. Of course a transition from Γ_3' could give a contribution with a decay time in the nsec range.

Our decay time measurements give a splitting of 5 meV for the components of the 1750 Å emissionband in solid Xenon which is very different from the value in the gaseous phase from ref.1. Furthermore these experiments show that most of the excitation energy is transfered by relaxation processes into a rather long living state which has to be taken into account in processes where energy transfer, relaxation or stimulated emission are involved.

To study relaxation processes from higher excited inital states to the radiative states optical excitation with monochromatic light is necessary. Therefore decay time measurements using the time structure of the synchrotron radiation of the storage ring DORIS at the Deutsches Elektronen Synchrotron in Hamburg are in progress.

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Table 1) Temperature dependent decay times of solid Xe according to equ.1

Wavelength [Å]	temperature [K]	decay times [nsec] τ_1	τ_2	$\frac{A_1(\tau_1)}{A_2(\tau_2)}$
	4 (+3)	3 ± 1	900 ± 50	
	5 (+3)	3 ± 1	800 ± 50	
1750 Å	10 (+3)	3 ± 1	700 ± 50	0.03
$\Delta\lambda$ = 100 Å	15 (+3)	3 ± 1	500 ± 50	0.04
	20 (+3)	3 ± 1	300 ± 20	0.08
	30 (+3)	3 ± 1	150 ± 20	0.03
	10	50 ± 10		
2600 Å	25	50 ± 10		
$\Delta\lambda$ = 100 Å	30	67 ± 10		

Table 2) Radiative decay times and energy splitting from the fit of the temperature dependence of τ_1 and τ_2 (equ.2)

E_{ab} [meV]	τ_{ra} [sec]	τ_{rb} [sec]	τ_{oa} [sec]	τ_{ob} [sec]
5 ± 1	(3 ± 1) x 10^{-9}	(900 ± 50) x 10^{-9}	2.7 x 10^{-8}	5 x 10^{-7}

Figure captions

Fig. 1, Measured decay curve for solid Xenon and fit according to equ.1 (solid line). The left insert shows the measured temperature dependence of the decay times and the fit according to equ.2 (solid lines). The right insert represents the luminescence emission curves for different times after deposition of the samples. For further details see text.

Fig. 2, Scheme for the levels and decay times involved in the interpretation of the temperature dependence. (see text.)

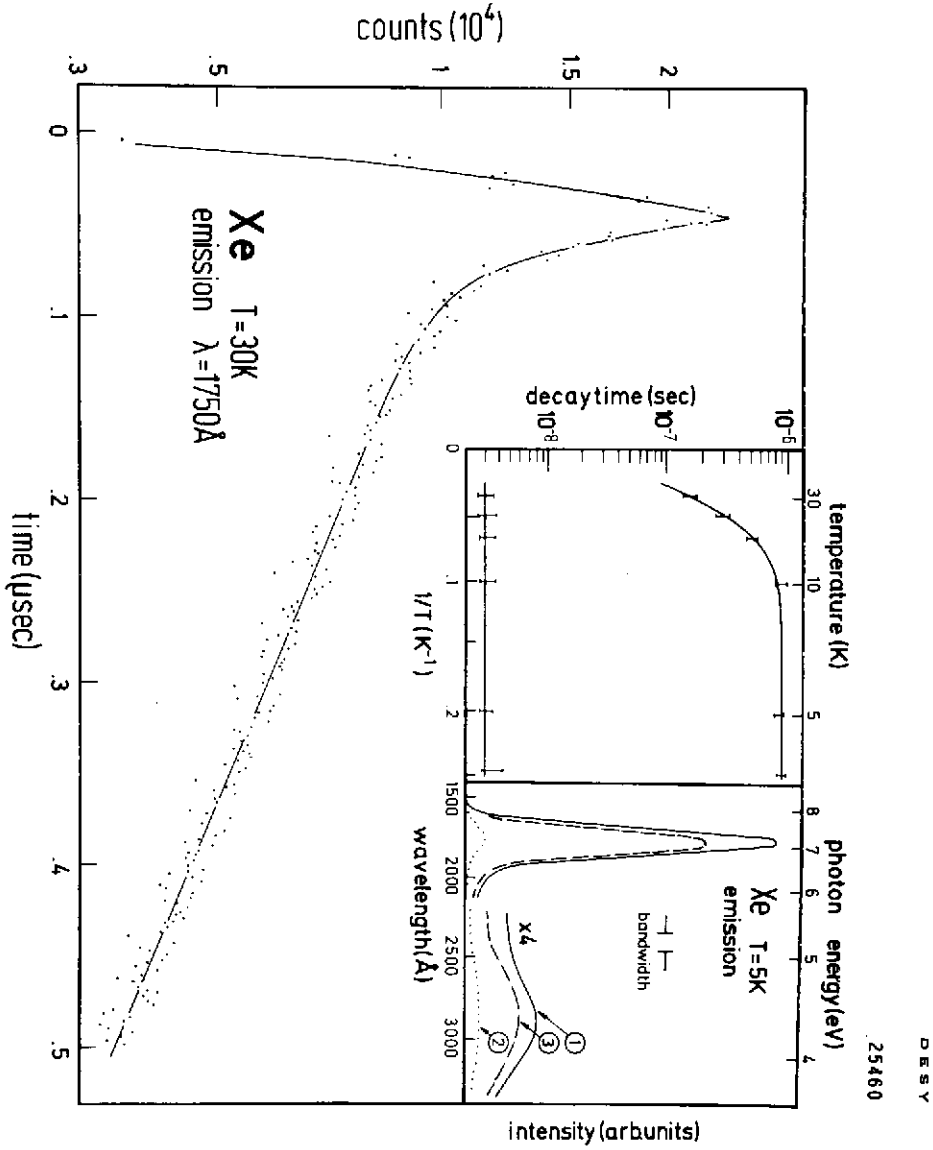

Fig. 1

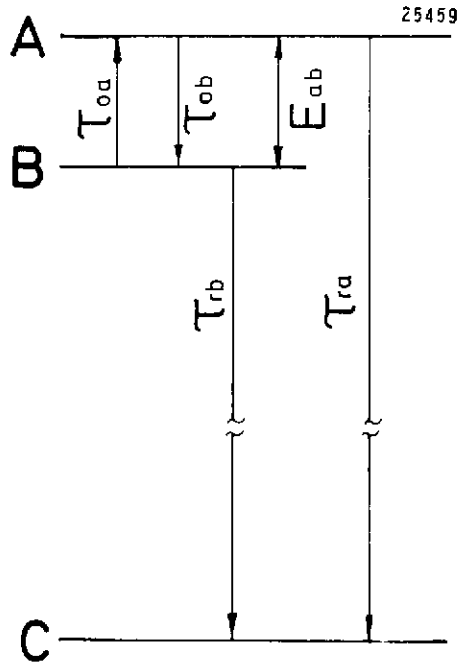

Fig. 2