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by

Ch. Ackermann
Deutsches Elektronen-Synchrotron DESY, Hamburg

R. Haensel and U. Hahn
Institut für Experimentalphysik der Universität Kiel

R. Brodmann, G. Tolkiehn and G. Zimmerer
II. Institut für Experimentalphysik der Universität Hamburg

2 HAMBURG 52 · NOTKESTIEG 1

PHOTOLUMINESCENCE AND EXCITATION SPECTROSCOPY OF RARE GASES

Ch. Ackermann, R. Brodmann[++], R. Haensel[+], U. Hahn[+], G. Tolkiehn[++],
and G. Zimmerer[++]

Deutsches Elektronen-Synchrotron DESY, Hamburg, Germany
Institut für Experimentalphysik der Universität Kiel,
Kiel, Germany[+]
II. Institut für Experimentalphysik der Universität Hamburg,
Hamburg, Germany[++]

Abstract

The photoluminescence bands of solid rare gases are discussed. The excitation spectra of the bands measured on samples with a "clean" surface show that the bulk quantum efficiency is independent of excitation energy in the region of excitonic excitation. Contamination leads to surface recombination and serves as a sink for excitons. Therefore the dynamics of free excitons can be studied from excitation spectra. Diffusive motion is assumed. Values for the diffusion lengths are deduced.

This paper mainly deals with the excitation spectra of the intrinsic luminescence bands of solid Ar, Kr, and Xe in the excitonic region of excitation. The aim is to get information about

(i) assignment of up to now not well understood emission bands

(ii) migration of excitation energy

(iii) dependence of quantum efficiency on excitation energy.

For excitation purposes the synchrotron radiation of the Deutsches Elektronen-Synchrotron DESY and of the storage ring DORIS, Hamburg, were used. Both the exciting and the luminescence light were monochromatized. Evaporated layers (thickness up to 25 000AE) were investigated. Because at a pressure of $\sim 10^{-9}$ Torr in the sample chamber contamination of the samples cannot be neglected, the time dependence of the excitation spectra was measured. By extrapolation to time $t = 0$, information about samples with a "clean" surface was obtained. Experimental details are given in (1).

Under monochromatic excitation, at temperatures around 5 K, the following bands appear: Ar (9.8 eV), Kr (8.25 eV), Xe (7.o5 eV) (2). They agree with the bands found with other kinds of excitation (3, 4) and are assigned to the diatomic molecular center (3) which results from self-trapping of an exciton (STE) or from self-trapping of a hole and capture of a free electron. At higher temperatures additional bands show up: the 7.6 eV band of Xe around 70 K in agreement with (5) and an Ar band at 11.2 eV around 25 K (2).

The excitation spectra (normalized to the incident intensity) of the low energy bands are shown in Fig. 1. The curves were measured immediately after sample preparation. During measurement the luminescence intensity decreased by 10 - 20 % from the extrapolated values for t = 0.

Within this uncertainty, the spectra yield the properties of samples with a "clean" surface. This is demonstrated for Kr in Fig. 2. The excitation spectra of the Kr band (Fig. 2a) were measured in time intervals indicated in the figure. In Fig. 2b, curve I (identical with the Kr curve of Fig. 1) is compared with extrapolated values of the luminescence intensity (crosses). A detailed analysis (1) of the results of Fig. 2a yields a relatively large decrease of luminescence until 1 to 2 monolayers of contamination are reached. Then the rate of change gets smaller until nearly static curves are obtained (like curve V).

The decrease of luminescence due to contamination is much more drastic for excitation in the absorption maxima (small penetration depth of light) than for excitation in the tails of absorption maxima (large penetration depth). In this way the pronounced minima of the excitation spectra corresponding to absorption maxima (2, 6) originate.

Fig. 3 presents the excitation spectra of both Xe bands in the temperature region of coexistence (~70 K). At low temperatures, the 7.6 eV band, and around 80 K the 7.05 eV band were found to be absent in agreement with (5). The overall shape of the curves differs from the Xe spectrum of Fig. 1 because of contamination.

The 7.6 eV band is hardly induced when exciting the n = 1 exciton. It is efficiently induced when exciting in the energy region of the n = 2 exciton. In this region of excitation both bands compete with each other. At first sight this result seems to support the assignment of the 7.6 eV band to the radiative decay of the n = 2 STE given by Molchanov (7). However, around 80 K (when the 7.05 eV band is absent) the 7.6 eV band is efficiently excited also at the low energy tail of the n = 1 exciton. Therefore it is still uncertain whether the 7.6 eV band of Xe originates from another luminescence center as the 7.05 eV band (5) or not (7).

In the region of excitonic excitation the excitation spectra are given by

$$Y \sim (1-R) \cdot \eta \cdot \frac{1}{J} \cdot \frac{1}{\tau} \cdot \int_0^d n(x) dx \qquad (1)$$

(J: intensity of incident light, R: reflectivity, τ : free exciton life time limited by self trapping, η : bulk quantum efficiency, n(x): steady state concentration of free excitons at distance x below the surface, d: film-thickness). n(x) is influenced by surface recombination. Two types of energy transfer to the surface are regarded:

(i) diffusion of free excitons

(ii) long range dipole interaction of excitons and the contaminant.

The excitation spectra can be calculated with both assumptions. Each theory allows to fit the experiment. From photoluminescence, at the present stage we cannot exclude one of the processes (1). Because photoelectric emission data support exciton diffusion (8), the diffusion model is discussed here. Under steady state conditions, n(x) is obtained from the diffusion equation

$$D \cdot \frac{d^2 n}{dx^2} = \frac{n(x)}{\tau} - J \cdot \alpha \exp(-\alpha x) \qquad (2)$$

(D: diffusion coefficient, α: absorption coefficient). The influence of contamination is introduced by the boundary conditions (9)

$$D \cdot \left(\frac{dn}{dx}\right)_{x=0} = n(0) \cdot S \quad ; \quad D \cdot \left(\frac{dn}{dx}\right)_{x=d} = -n(d) \cdot S^* \qquad (3)$$

(S: surface recombination velocity). Because neither η nor τ are known, n(x) and the luminescence intensity are calculated in relative units under the assumption that η and τ are independent of excitation energy.

The excitation spectra of samples with a "clean" surface are well reproduced by eq. (1) with S = 0 used for the calculation of n(x). This is shown for Kr in Fig. 2b (upper curves). The absolute values of the S = 0 calculation and experiment are fitted one to another around 10.5 eV. The minima in the experimental spectrum of a "clean" sample are caused by reflectivity.

The assumption of η and τ being constant seems to be correct in the region of excitonic absorption. The measured increase of the excitation spectrum around 11 eV may be due to excitation with higher order light ($h\nu \sim 2\ E_g$). Around $h\nu \sim 2\ E_g$ the luminescence yield substantially increases due to electron-electron scattering (10).

Surface quenching is gradually introduced in the calculation by increasing values of S. With $S \gtrsim 100\ v_D$ (v_D: diffusion velocity) the influence of the surface saturates. Then the only adjustable parameter of the calculation is the diffusion length $L_o = \sqrt{D \cdot \tau}$.
From the fit in Fig. 2b (lower curves) L_o = 200 Å for the Kr excitons is found. The deduced value of L_o sensitively depends on the α-values used in the calculation. We used the data of Baldini (11). With the absorption data of Ref. (12) L_o = 600 Å is obtained. The situation is similar for the other rare gases. We obtain L_o = 50 Å for Ar and L_o = 150 Å for Xe.

At higher temperatures and for annealed samples the structures of the excitation spectra get much more pronounced (like in

Fig. 3). This results in larger values for L_o (e.g. 500 Å to 1000 Å for Xe at 45 K). The reason for this behaviour is unknown. Perhaps L_o is connected to crystallite size.

The diffusion lengths deduced from excitation spectra roughly agree with values deduced from photoemission (8, 13).

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Figure Captions

Fig. 1 Excitation spectra of the 9.8 eV Ar, 8.25 eV Kr, and 7.05 eV Xe luminescence bands.

The peak positions of excitonic absorption maxima ($n = 1,2,3$ members of the $\Gamma(3/2)$ and $n' = 1,2,3$ members of the $\Gamma(1/2)$ series and the band gaps (14) are indicated.

Fig. 2

a) Time dependence of the excitation spectrum of the Kr band due to contamination. Curve IV and V coincide around 10 eV and 10.5 eV.

b) Comparison between experiment and model calculation (Kr band). I: "clean" surface, V:contaminated surface. The relative values are consistent.

Fig. 3 Excitation spectra of the Xe 7.05 eV and 7.6 eV bands at 70 K.

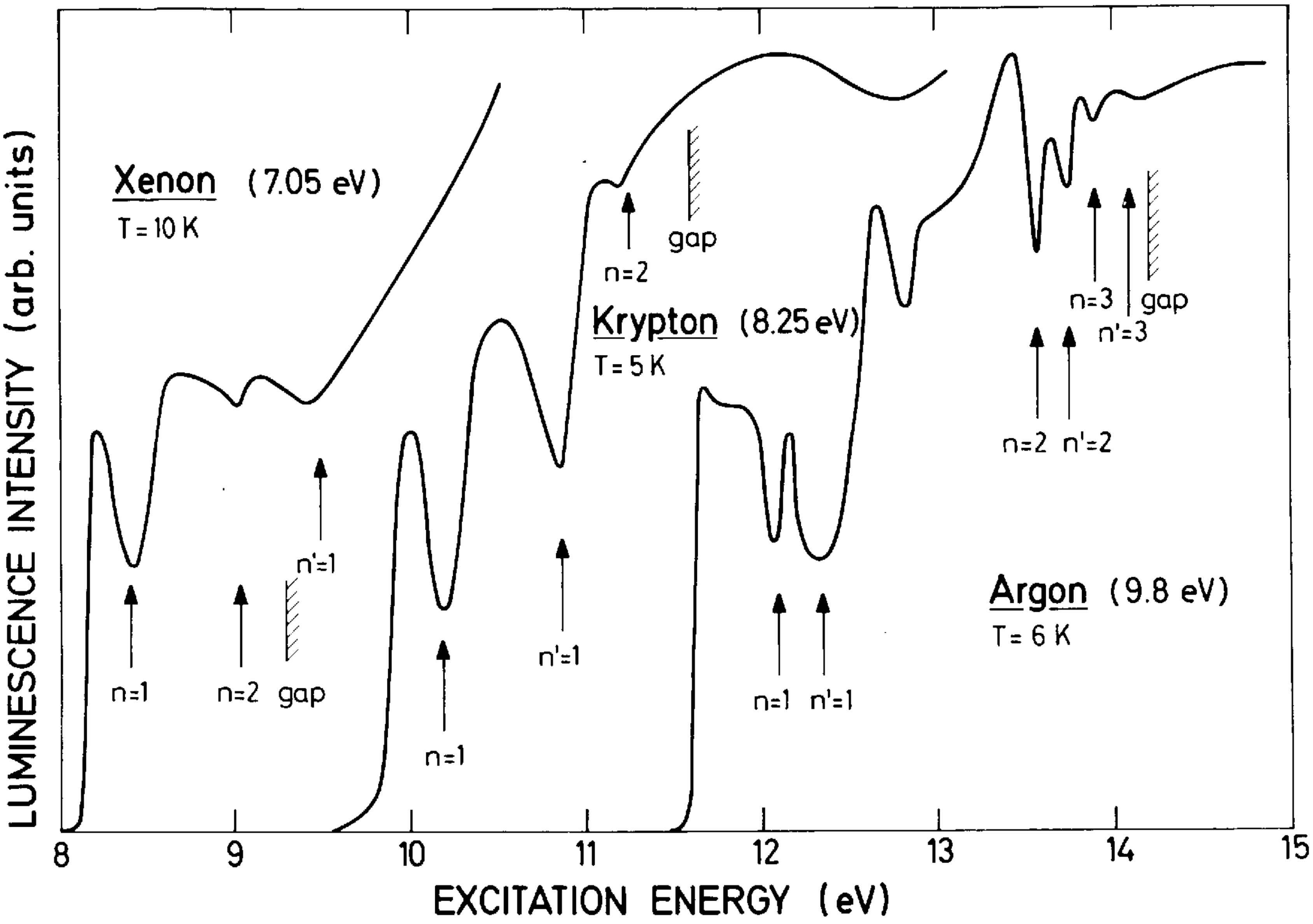
Xenon (7.05 eV)
T = 10 K
Krypton (8.25 eV)
T = 5 K
Argon (9.8 eV)
T = 6 K
n=1
n=2
gap
n'=1
n=1
n'=1
n=2
gap
n=1
n'=1
n=2
n'=2
n=3
n'=3
gap
LUMINESCENCE INTENSITY (arb. units)
EXCITATION ENERGY (eV)
8
9
10
11
12
13
14
15

Fig. 1

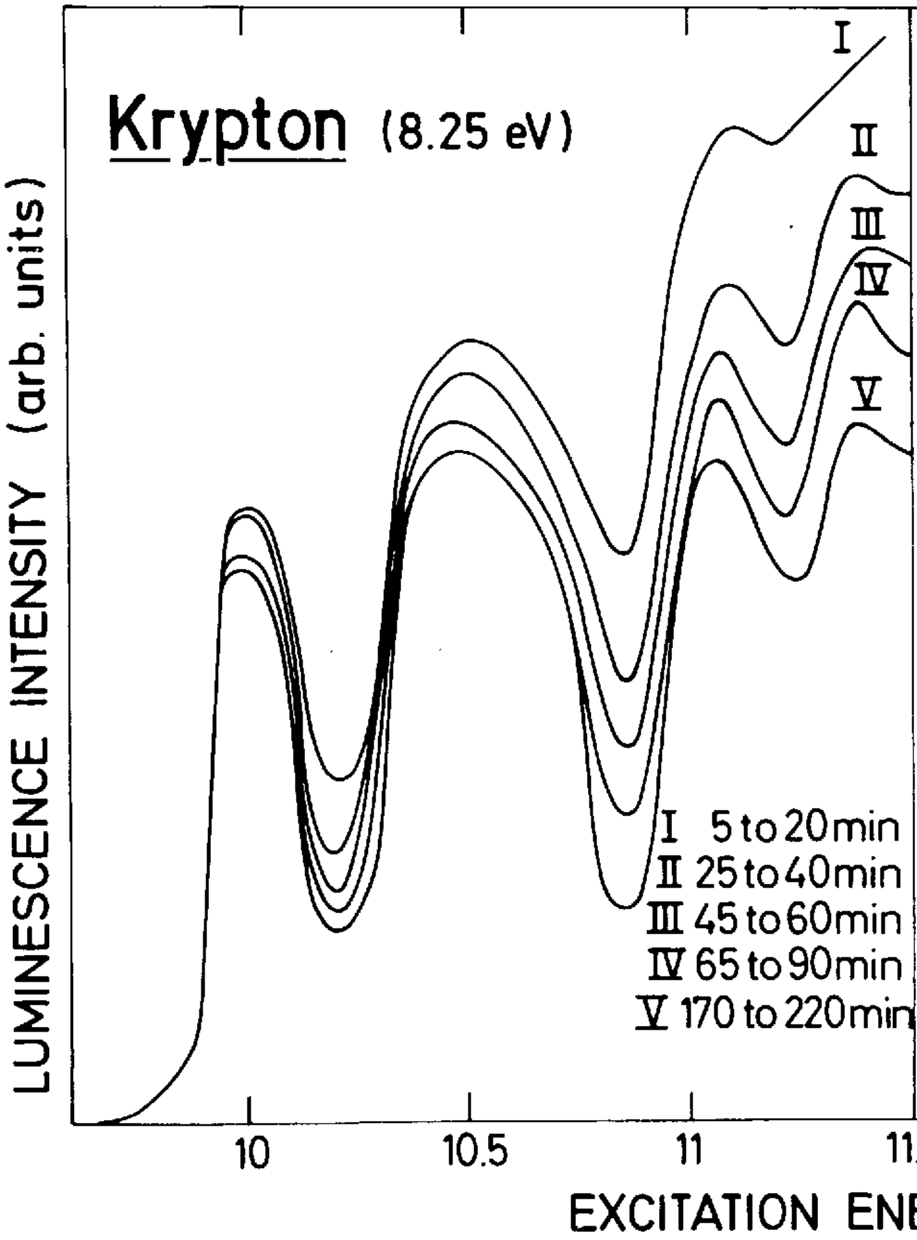
Krypton (8.25 eV)
LUMINESCENCE INTENSITY (arb. units)
I
II
III
IV
V
I 5 to 20 min
II 25 to 40 min
III 45 to 60 min
IV 65 to 90 min
V 170 to 220 min
10
10.5
11
11.5
EXCITATION ENERGY (eV)

Fig. 2a

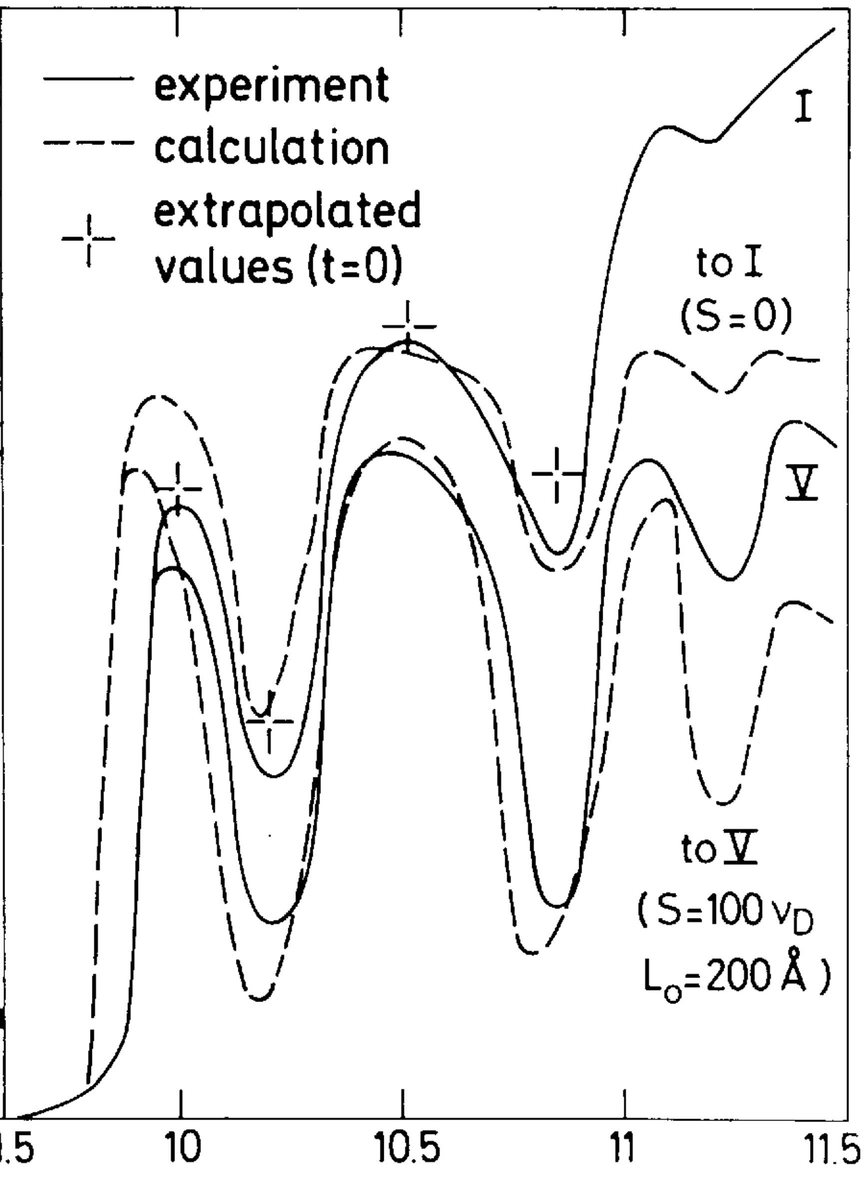
experiment
calculation
extrapolated values (t=0)
I
to I (S=0)
V
to V (S=100 v_D L_o=200 Å)
10
10.5
11
11.5

Fig.2b

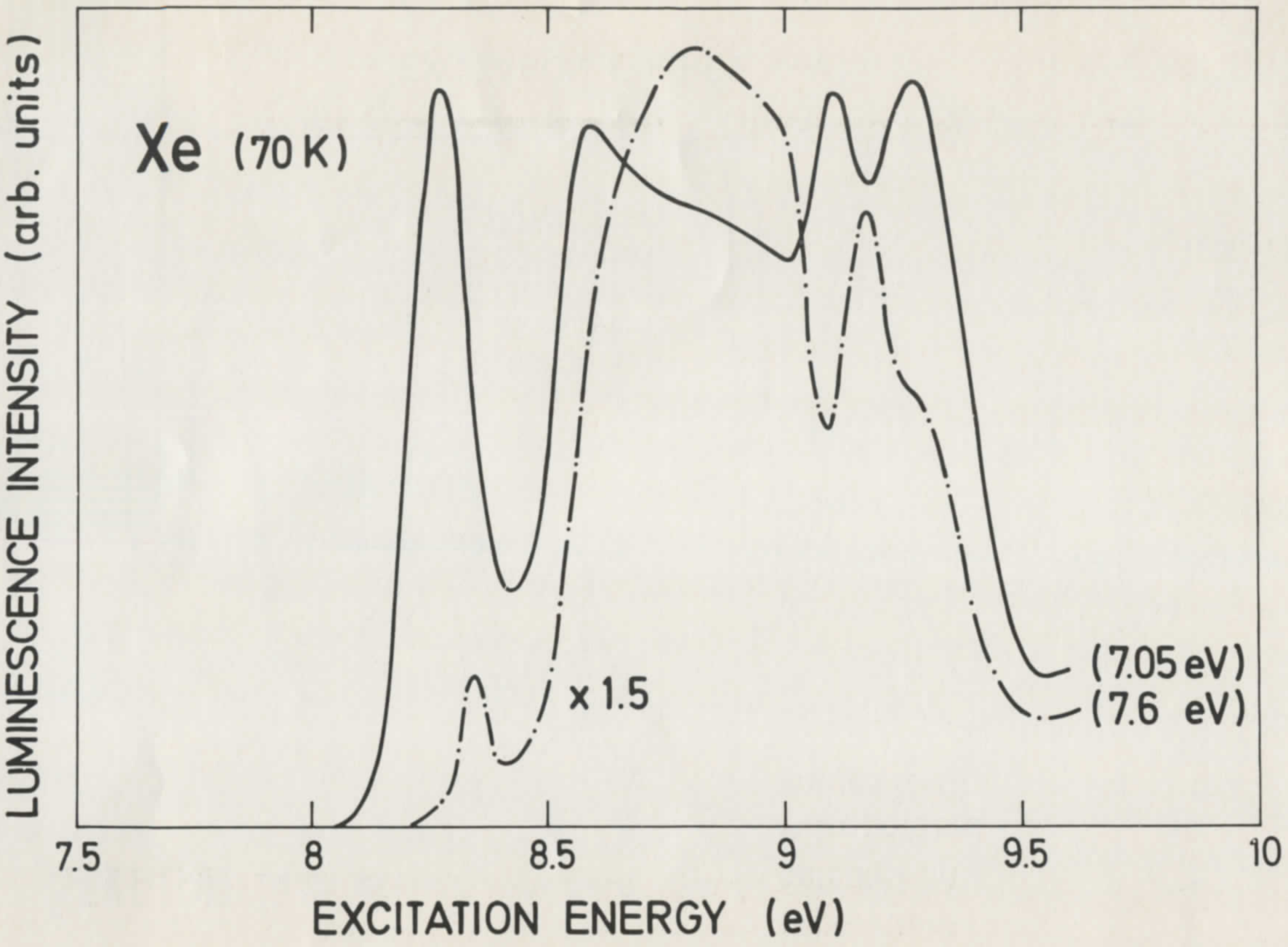
Xe (70 K)
LUMINESCENCE INTENSITY (arb. units)
EXCITATION ENERGY (eV)
7.5
8
8.5
9
9.5
10
x 1.5
(7.05 eV)
(7.6 eV)

Fig. 3