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Vibrational Relaxation and Hot Luminescence of Ne_2^* Centers in Solid Neon

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Abstract

Hot luminescence of Ne_2^* centers (molecular type self-trapped excitons) in solid Ne was measured under state selective excitation using synchrotron radiation. The luminescence spectra were analysed with the aid of a new theory on vibrational relaxation of the Ne_2^* centers. It was possible to show that the rate of relaxation is slower for centers located at the surface than for centers in the bulk of the Ne solid. In combination with a direct measurement of the lifetimes (1ns for $^1\Sigma_u^+$; 5 µs for $^3\Sigma_u^+$), absolute values for the relaxation rates were obtained. They range between $6.6\times10^4 s^{-1}$ (bulk) and $6.6\times10^3 s^{-1}$ (surface).

Die Lumineszenz schwingungsangeregter Ne_2^*-Zentren (molekülartige autolokalisierte Exzitonen) in festem Ne wurde mit zustandsselektiver Anregung durch Synchrotronstrahlung untersucht. Mit Hilfe einer neuen Theorie der Schwingungsrelaxation von Ne_2^*-Zentren wurde die Spektralverteilung analysiert. Hierdurch konnte gezeigt werden, daß die Relaxationsrate der Zentren an der Oberfläche bedeutend kleiner ist als im Innern des Ne-Festkörpers. In Kombination mit einer Messung der Lebensdauern (1ns für den $^1\Sigma_u^+$; 5 µs für den $^3\Sigma_u^+$-Zustand) konnten die Relaxationsraten absolut bestimmt werden. Sie liegen zwischen $6.6\times10^4 s^{-1}$ im Innern und $6.6\times10^3 s^{-1}$ an der Oberfläche des Festkörpers.

1. Introduction

Vibrational relaxation of molecular centers embedded in a matrix is a sensitive measure of the coupling between the local oscillator and lattice vibrations. In the case of strong electron-phonon coupling, the relaxation rates are usually of the order of $10^{12}\ s^{-1}$. The theory of relaxation is developed in [1 - 6]. A direct calculation of relaxation rates, however, is up to now a severe problem. For rare gas molecular centers (R_2^* centers) in rare gas crystals, the basic crystal properties and the interatomic potentials are known well enough to attack the calculation of relaxation rates with realistic physical models.

R_2^* centers resemble rare gas excimers embedded in a matrix [7]. They have a repulsive ground state, $^1\Sigma_g^+$, and bound excited states, $^3\Sigma_u^+$ and $^1\Sigma_u^+$, which, in the gas phase, terminate at $^3P_2$ and $^3P_1$ excited atoms [8]. The R_2^* centers are interesting from different points of view,

(i) they are created via self-trapping of excitons and are the lowest intrinsic excited states of rare gas crystals

(ii) they play an important role in energy dissipation processes in these simple molecular solids

(iii) with decreasing atomic weight, the vibrational frequency Ω of the R_2^* centers exceeds more and more the Debye frequency of the crystal (Xe: $\Omega \approx 3\ \omega_D$; Ne: $\Omega \approx 9\ \omega_D$) [9 - 11], and vibrational relaxation is slowed down from the pico-second range in Xe [12] to micro-seconds in Ne (this paper).

With decreasing vibrational relaxation rates, the phenomenon of hot luminescence (HL) gets stronger. HL stems from those centers which are not in thermal equilibrium with the crystal. In solid Ne, HL of Ne_2^* exceeds ordinary luminescence (OL) of Ne_2^* [5,12]. The spectral distribution of HL is a sensitive probe for the process of vibrational relaxation. The Ne_2^* center in solid Ne may be regarded as a model system to test theories of vibrational relaxation.

A first attempt to calculate relaxation rates for Ne_2^* stems from Martin [13]. He treated the problem as a series of resonant transfer collision of the vibrating center in a linear chain of atoms (based on the assumption that the coupling to the lattice is important only for longitudinal modes in the direction of the molecular axis). He obtained relaxation times below $6 \cdot 10^{-12}$ s.

Yakhot [5] and Yakhot et al [4] treated vibrational relaxation of Ne_2^* as a multiphonon process. Due to the anharmonicity of the Ne_2^* oscillator, relaxation is fast between high vibrational levels and slowed down dramatically at low vibrational levels. Numerical results are discussed below. Yakhot et al [4] concluded that the main contribution to luminescence of Ne_2^* in solid Ne stems from the third vibrational level. The Franck-Condon factor of the transition $^3\Sigma_u^+(N=3) \rightarrow {}^1\Sigma_g^+$ indeed gives a qualitatively reasonable description of the Ne_2^* luminescence measured by Packard et al [14] but cannot account for the results of this paper.

More recently, the luminescence of the relaxing Ne_2^* center was calculated simulating the center by a classical damped Morse oscillator [12]. The damping constant, W_d is a measure of vibrational relaxation and was determined from a fit of experimental luminescence spectra. Kink et al obtained $W_d \approx .6\,\Gamma$, where Γ is the radiative decay rate. With this model it was only possible to calculate the envelope of the luminescence spectrum but not the oscillatory structure of bound-free emission.

In another attempt, Grigorashchenko et al [15] tried to explain fine structures in Ne_2^* luminescence by Franck-Condon factors of N=1 ... N=6 of $^3\Sigma_u^+$. However, the linkage of the luminescence of individual vibrational levels by the relaxation rates was not treated explicitely.

In this paper, the results of a recent quantum mechanical theory of vibrational relaxation of Ne_2^* by Selg [16] are compared with photoluminescence experiments. The main results of the theory which can also be applied to other rare gas crystals, are outlined in the next section. Then experimental results of time and spectrally resolved luminescence measurements are presented and compared with theory. It turns out that vibrational relaxation rates of Ne_2^* centers at the surface and in the bulk are quite different. Generally, good agreement between theory and experiment is obtained.

2. Calculation of vibrational relaxation of Ne_2^* in solid Ne

The theory developed by Selg [16] uses the so-called 'double adiabatic' approximation which is based on the fact that $\Omega \gg \omega_{\vec{k}_r}$ ($\omega_{\vec{k}_r}$: frequency of lattice vibration with wave vector $\vec{k}$ of phonon branch r). Within this approximation, the dependence of vibrational state N of the local oscillator on a lattice vibration is described by an adiabatic energy surface. In Fig. 1, the energies of the (local) vibrational levels N, N-1 are drawn schematically as a function of the configuration coordinate, q, of the crystal oscillator $\omega_{\vec{k}_r}$. The process of vibrational relaxation N → N-1 is calculated by Selg using a model composed of tunneling from one surface to the other one (step 1 in Fig. 1), and thermalization of the crystal oscillator within the new level of the local oscillator (step 2).

At T = 0K, the vibrational relaxation rate linking together level N (energy E_N) and level N-1 (energy E_{N-1}) reads

$$W_{N \to N-1} = \frac{A \cdot N}{\Omega_N^3 (\Omega_N - 2\bar{\omega})^2} \qquad (1)$$

The factor A is determined by the interatomic potential Ne — Ne, the reduced mass of the center, the phonon spectrum, and the Debye frequency. Ω_N is the energy difference $E_N - E_{N-1}$, and $\bar{\omega}$ is defined via $(\Omega_N - 2\bar{\omega})^{-2} = \langle (\Omega_N - 2\omega_{\vec{k}_r})^{-2} \rangle$ ($\bar{\omega}$ = 3.5 meV for Ne_2^*/Ne). In the case of Ne, Eq.(1) can be used up to the melting point, T_m, because $T_m \ll \Theta_D$ (Debye temperature).

In his calculation, Selg approximated the Ne_2^* potential by the $^3\Sigma_u^+$ potential of the free molecule given by Berman and Kaldor [11] with its dissociation energy of .4 eV. However, as a consequence of a potential hump at larger internuclear distances, up to N ≈ 10, the potential is well described analytically by a Morse potential with Ω = 51.5 meV and D_e = .64 eV. The calculated transition probabilities are given in Table 1 and compared with Yakhot's results [4] . A striking discrepancy is found.

Selg [16] defines a quantity τ_s which describes vibrational relaxation from $N = N_{max}$ to N = 0,

$$\tau_s = \sum_{N=1}^{N_{max}} W^{-1}_{N \to N-1} \qquad (2)$$

He obtains $\tau_s = 3 \cdot 10^{-6}$ s for Ne_2^*/Ne which is shorter by ∿ 7 orders of magnitude than the corresponding result of Yakhot.

Calculation of stationary luminescence spectra is now relatively simple. The spectral distribution of luminescence of each vibrational level is calculated according to the semi-classical Franck-Condon principle. For each vibrational level, the branching between luminescent decay and vibrational relaxation is given by $\Gamma_R^N / W_{N \to N-1}$, Γ_R^N being the radiative decay rate of the N'th vibrational level. Under stationary conditions ($\dot{n} = 0$), the occupation number n of each level, N, is obtained with a constant pumping term of the highest vibrational level. Selg even included the dependence of the radiative lifetime on N for a Morse type oscillator, which, however, is only a weak function of N, $\Gamma_R^N = f(N) \cdot \Gamma_R^0$. Finally, the contributions of all vibrational levels are summed up.

The spectral distribution of luminescence thus sensitively depends on the ratio Γ_R^0/W , $W = \tau_s^{-1}$. In Fig. 2, curves for different values of this ratio are given. Good agreement with the measurement of Schuberth and Creuzburg [17] is obtained with $\Gamma_R^0/W = 3$. Taking into account $\tau_s = 3 \cdot 10^{-6}$ s calculated independently, this corresponds to a radiative lifetime $\tau_R = 1/\Gamma_R^0 = 1$ µs. In this paper we present experimental values for τ_R which are larger and thus lead to a modification of τ_s.

The luminescence spectra presented in this paper are of the type represented by larger values of Γ_R^0/W which is equivalent to smaller relaxation rates in our samples.

3. Experiment

3.1 Technical details

The measurements were carried out at the experimental station Superlumi at HASYLAB Hamburg. The entire set-up has been described previously [18,19]. Spectrally selected synchrotron radiation with a band pass of .25 nm was used to excite the sample in the wave length range 20 - 73 nm. Luminescence was analysed by a VUV-monochromator with a band pass of .8 nm. The pulsed structure of synchrotron radiation, which consists of sharp light flashes (fwhm = 130 ps) with a repetition rate of 1 MHz was exploited to provide time resolved data. With a channel-plate detector and the fast timing electronics used, time resolution to about 100 ps was obtained.

The solid Ne samples were prepared from Ne gas with a nominal purity of 99.99 %. This gas was condensed on a LiF substrate cooled to 6.3 K. The film thickness was determined from observation of the interference effects in the reflected light during deposition. The gas handling system and the sample chamber were operated under UHV conditions.

3.2. Experimental results

As is well known from earlier experiments [12,14,17,20] the intrinsic luminescence of solid Ne contains two different contributions,

(i) luminescence of the atomic type self trapped exiton (Ne^* center) at 74,2 nm.

(ii) luminescence of the molecular type self trapped exciton (Ne_2^* center) extending from ∿ 75.5 nm to ∿ 90 nm.

Fig. 3a shows typical emission spectra, excited with photons in the n = 2 bulk exciton region (20.2 eV) and the n = 1 surface exciton region (17.2 eV) (surface and bulk excitons of solid Ne are described in detail in Ref. 21). The photoluminescence spectra are compared with literature results obtained under x-irradiation of a bulk Ne sample [17]. The different substructures of the spectrum measured by Schuberth and Creuzburg [17] are more or less smeared out in the photoluminescence spectra. This is only to a minor extend due to the finite band pass of .8 nm used here. The physical reasons are discussed below.

The amount of the atomic type luminescence (Ne^*) was separated from the molecular type luminescence (Ne_2^*) in the following way. The shape of Ne^* emission was approximated by a Gaußian curve (the fwhm of which is mainly caused by the bandpass of analysis). The Gaußian curve was fitted to Ne^* emission at the high energy side, where definitely no Ne_2^* emission occurs. Then the Ne^* luminescence was subtracted from the measured spectrum. As an example, in Fig. 3b both contributions are shown corresponding to curve 2 in Fig. 3a. It should be mentioned here that the ratio of Ne^* and Ne_2^* luminescence is a sensitive function of bulk or surface excitation [22]. Under primary excitation of the n = 1 surface exciton, Ne^* luminescence exceeds by far Ne_2^* emission. There are close similarities to solid Ar [23]. In this paper, however, we restrict ourselves to the spectral behaviour of Ne_2^* luminescence.

Fig. 4 displays the dependence of Ne_2^* emission upon the photon energy of primary excitation. Under primary excitation of n = 1 surface excitons, the maximum of Ne_2^* emission is at higher energies (16.5 eV) and the tail to lower energies is very weak. Primary excitation of bulk states (e.g., n = 2 excitons, E_{ex} = 20.2 eV; interband transitions with E_{ex} = 21.9 eV or 36.5 eV) leads to spectra with a more pronounced tail and a somewhat shifted maximum (16.35 eV). Primary excitation of n = 1 bulk excitons yields a curve between the cases shown in Fig. 4.

In Fig. 5, a typical decay curve of Ne_2^* luminescence is shown (interband

excitation at 21.9 eV, photon energy of luminescence 16,1 eV). Such curves were measured for different combinations of excitation and luminescence energy. Numerical results are collected in Table 2. A fast ($10^9 s^{-1}$) and a slow (1 ... $0.2\times10^6 s^{-1}$) decay rate are clearly observed and ascribed to the $Ne_2^*\ {}^1\Sigma_u^+$ and $Ne_2^*\ {}^3\Sigma_u^+$ state. Whereas the value of the fast rate is independent from the photon energy of excitation and luminescence, the value of the slow rate is a complex function of both quantities. We cannot expect one unique experimental value for the ${}^3\Sigma_u^+$ decay rate because luminescence is a superposition of many emitting vibrational levels which, on the other hand, are coupled by vibrational relaxation. As we shall see below, the relaxation rate is a function of primary excitation and crystal quality. So, the smallest decay rate ever measured in our experiments may be taken as a lower limit for the radiative lifetime, $\tau_{rad}({}^3\Sigma_u^+) \gtrsim (5\pm1)\mu s$. This is in good agreement with gas phase data [24].

Additional to the fast and slow decay rate, an intermediate is observed, too (∿ $10^8 s^{-1}$). Its amplitude depends on the excitation energy. It is very weak under bulk excitation but is clearly observable under surface sensitive excitation. The origin of this decay rate is unclear up to now.

4. Comparison between theory and experiment

In Fig. 2 and Fig. 3, structured luminescence spectra of bulk samples (x-irradiation) [17] and photoluminescence results of thin layers (1 ...10μm) under bulk and surface excitation are compared with theory [16]. The different experimental results are well reproduced by theory by simply changing the ratio Γ_R^0/W (Table 3). As the radiative decay rate Γ_R^0 of the Ne_2^* center is expected to be approximately the same in all samples, the different values of the ratio and hence the different shapes of the spectra are due to different rates of vibrational relaxation, characterized by the quantity $W = \tau_s^{-1}$. Compared to the bulk samples of Schuberth and Creuzburg with crystallites of ∿ 1μm [25], relaxation is slowed down by a factor of 3 in evaporated layers under bulk excitation. This favours emission from higher vibrational levels. It is slowed down by another factor of ∿ 3 under surface excitation of layers. These conclusions hold independently from the actual value of the radiative decay rate Γ_R. The tendency of slowing down vibrational relaxation when the luminescent center is positioned at the surface of the sample is in good agreement with similar results on Ar [23].

As we have measured the radiative decay rate directly, we are able to deduce experimental values of W from the ratios Γ_R^0/W. Results are listed in Table 3. Note, that our value of $\Gamma_R^0 = 2\cdot 10^5 s^{-1}$ ($\tau_R = 5\cdot 10^{-6} s$) is a lower limit, which may be near to the correct value because it corresponds well to gas phase results [24]. In the bulk samples of Schuberth and Creuzburg, the experimental τ_s is larger by a factor of 5 compared to Selg's result [16]. In view of the difficulties encountered in a direct calculation of vibrational relaxation rates, the agreement between theory and experiment is quite satisfactory.

The theoretical value of τ_s was calculated for the ideal crystal and thus cannot be compared with the experimental value obtained for centers at the surface. A theoretical analysis of the influence of structural changes around the relaxing center on Eq. (1) seems to us an achievable as well as a worthwhile goal for future work.

The experimental results clearly show that the luminescence spectra of Ne_2^* centers sensitively depend on sample preparation. Bulk excitation of evaporated layers results in spectra which yield vibrational relaxation rates between surface values and bulk values of samples with large crystallites. The behaviour of evaporated layers obviously indicates that the crystallites are very small ("large inner surface"). In general, in solid Ne, the balance between vibrational relaxation and radiative decay of Ne_2^* centers is a direct probe of the sample quality.

Finally, we want to compare the theoretical results of Yakhot et al [4] and Selg [16] (Table 1). The discrepancy in τ_s is not the only point which should be stressed. In the theory of Yakhot et al, the rates $W_{N \rightarrow N-1}$ change by ∿ two orders of magnitude for neighbouring vibrational levels, in Selg's theory only by a factor of ∿ 2. Therefore, Selg's approach predicts a contribution of some neighbouring vibrational levels to luminescence, whereas Yakhot's theory predicts fast relaxation unless excitation sticks in one vibrational level which then radiates. Then the spectral distribution of luminescence should reflect the oscillatory structure of the FC-factor of that particular level whereas in Selg's theory such structures are smeared out. From this point of view, the experimental photo-luminescence spectra favour Selg's theory.

The overall behaviour of Ne_2^* luminescence especially under surface sensitive excitation can be explained with the theory of Yakhot et al only, if structural changes in the sample introduce changes of the relaxation rates by several orders of magnitude. Indeed, this theory is extremely sensitive to fractional changes of some relevant parameters as has been pointed out recently [23] . The moderate

changes of relaxation rates needed to explain the experimental results with Selg's theory seem to be much more probable.

5. Conclusions

In this paper, photoluminescence spectra of Ne_2^* centers in solid Ne are presented and compared with experimental results under x-irradiation. Though the spectra are different they can be explained consistently within the framework of a new theory on vibrational relaxation of a molecular center. The key in understanding the experimental results is the sensitivity of the coupling between the local oscillator and the lattice modes on structural changes. This effect is most clear for vibrational relaxation of Ne_2^* centers at the surface of the sample and in the bulk.

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Figure Captions

Fig. 1 Model for vibrational relaxation after Selg [16]. N is the vibrational quantum number of the local oscillator . Ω_N is the energy difference of two adjacent vibrational levels. ΔE is the barrier height for tunneling from the surface N to surface N-1. $\omega_{\vec{k}_r}$ is the quantum of a crystal oscillator with coordinate $q_{\vec{k}_r}$

Fig. 2 Full curves are calculated luminescence spectra of Ne_2^* centers in solid Ne with different ratios of radiative decay rate vs vibrational relaxation rate, taken from [16] . The dashed curve is an experimental result from Schuberth and Creuzburg [17].

Fig. 3a Different luminescence spectra of solid Ne. Curve 1 is obtained under x-irradiation [17]. Curves 2 and 3 are photo-luminescence spectra under bulk and surface sensitive excitation.

3b Separation of the luminescence of solid Ne into the Ne^* and the Ne_2^* contribution (curve 2 from Fig. 3a)

Fig. 4 Comparison between experimental photo-luminescence spectra of Ne_2^* centers in solid Ne with theoretical results of Selg (full lines) [16] curve 1 and the corresponding experimental results correspond to bulk excitation of Ne layers. Curve 2 and the corresponding experimental result are obtained under surface sensitive excitation. E_{ex} : photon energy of excitation

Fig. 5 Decay curve of Ne_2^* luminescence in solid Ne (photon energy of excitation 21,9 eV, of analysis 16.1 eV) with the slow (here 3 μs) and the fast (1 ns) component (expanded scale). The insert gives a schematic potential curve diagram of the Ne_2^* center with the assignment of the decay components.

List of Tables

Table 1 Theoretical vibrational relaxation rates $W_{N \rightarrow N-1}$ of the N'th vibrational level of the Ne_2^* center in solid Ne after Selg [16] and Yakhot et al [4] . All rates are given in s^{-1}. The meaning of τ_s is explained in the text.

Table 2 Compilation of the different decay rates observed in Ne_2^* luminescence in solid Ne at 6.3 K with the assignment, and a corresponding gas phase value [24] . All rates are given in s^{-1}

Table 3 Compilation of the ratios radiative decay rate vs vibrational relaxation rate for different samples and excitation conditions. Absolute values of the vibrational relaxation rate, W_{exp}, are obtained with $\Gamma_R^o = 2\cdot 10^5\ s^{-1}$ and compared with the theoretical value of Selg [16]. All rates are given in s^{-1}.

Table 1

N	1	2	3	4	5	τ_s
$W_{N \rightarrow N-1}$ of Ref. [16]	$6,30\cdot10^5$	$1,58\cdot10^6$	$3,02\cdot10^6$	$5,18\cdot10^6$	$8,44\cdot10^6$	$3\cdot10^{-6}$s
$W_{N \rightarrow N-1}$ of Ref. [4]	$1\cdot10^{-1}$	$1\cdot10^2$	$2,5\cdot10^4$	$2,5\cdot10^6$	$1,25\cdot10^8$	∿ 10 s

Table 2

decay rate	numerical value	corresponding lifetime	assignment	corresponding gas phase values
fast	$(1\pm0,1)\cdot10^9 s^{-1}$	(1±.1) ns	$Ne_2^* \; {}^1\Sigma_u^+ \rightarrow {}^1\Sigma_g^+$	
intermediate	$(1\pm0,1)\cdot10^8 s^{-1}$	(10±1) ns	unclear	
slow	$2\cdot10^5 \ldots 10^6 s^{-1}$	1...5 μs	$Ne_2^* \; {}^3\Sigma_u^+ \rightarrow {}^1\Sigma_g^+$	5.2 μs (Ref. 24)

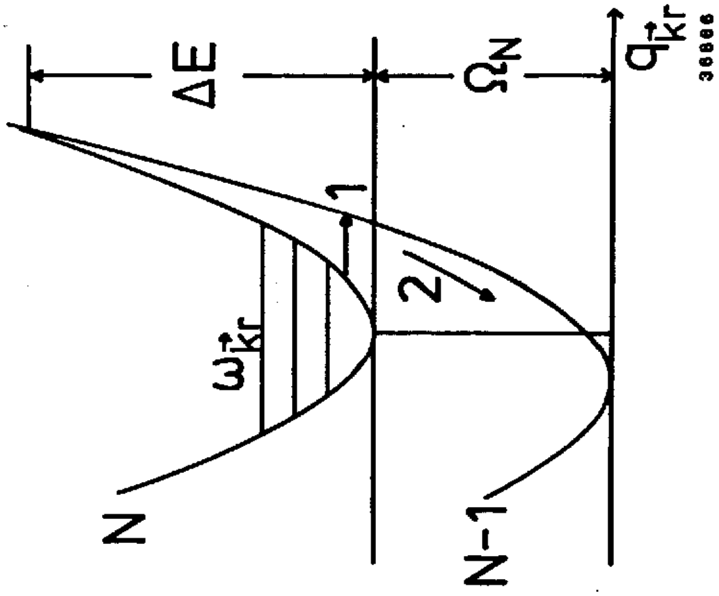

Figure 1

Table 3

sample	excitation condition	Γ_R^o/W	W_{exp}	W_{theory}
bulk [17]	bulk, x-irradiation	3	$6{,}6\cdot10^4$	$3{,}3\cdot10^5$
layer	photons, bulk	9	$2{,}2\cdot10^4$	
layer	photons, surface	30	$0{,}66\cdot10^4$	

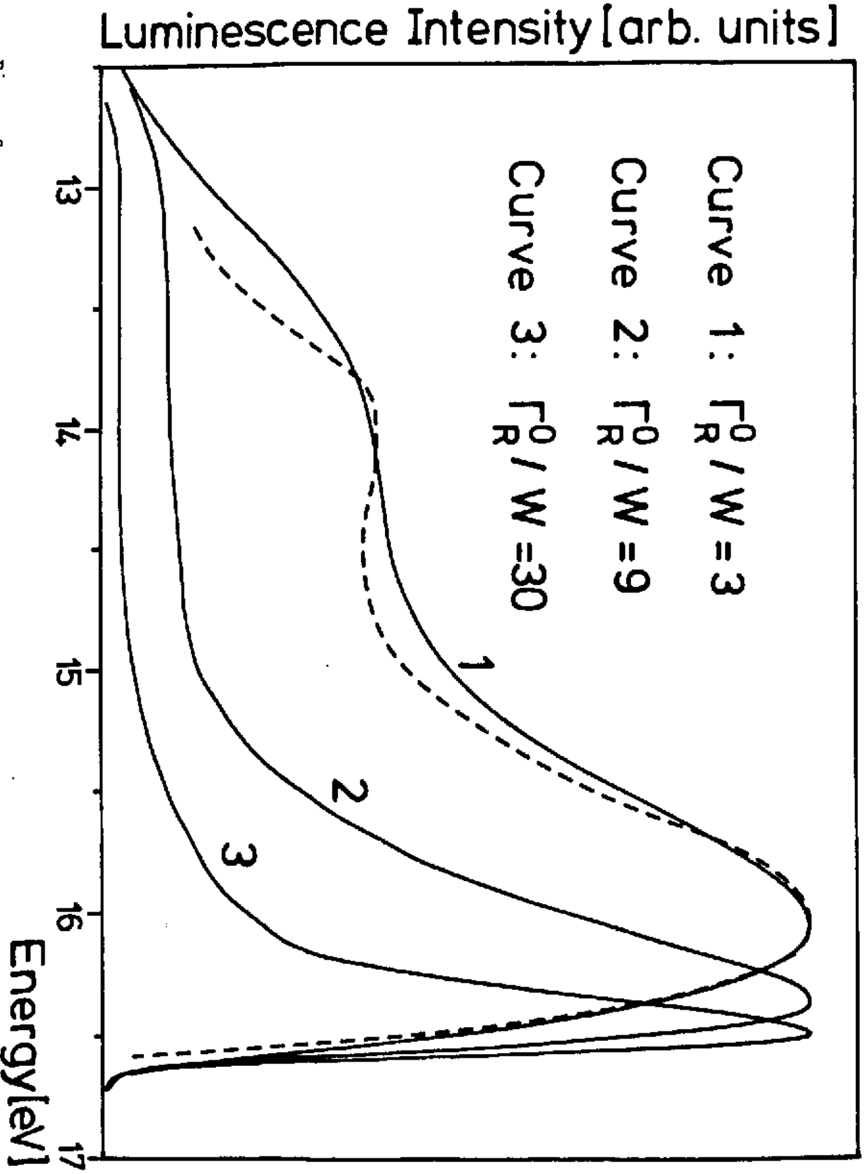

Figure 2

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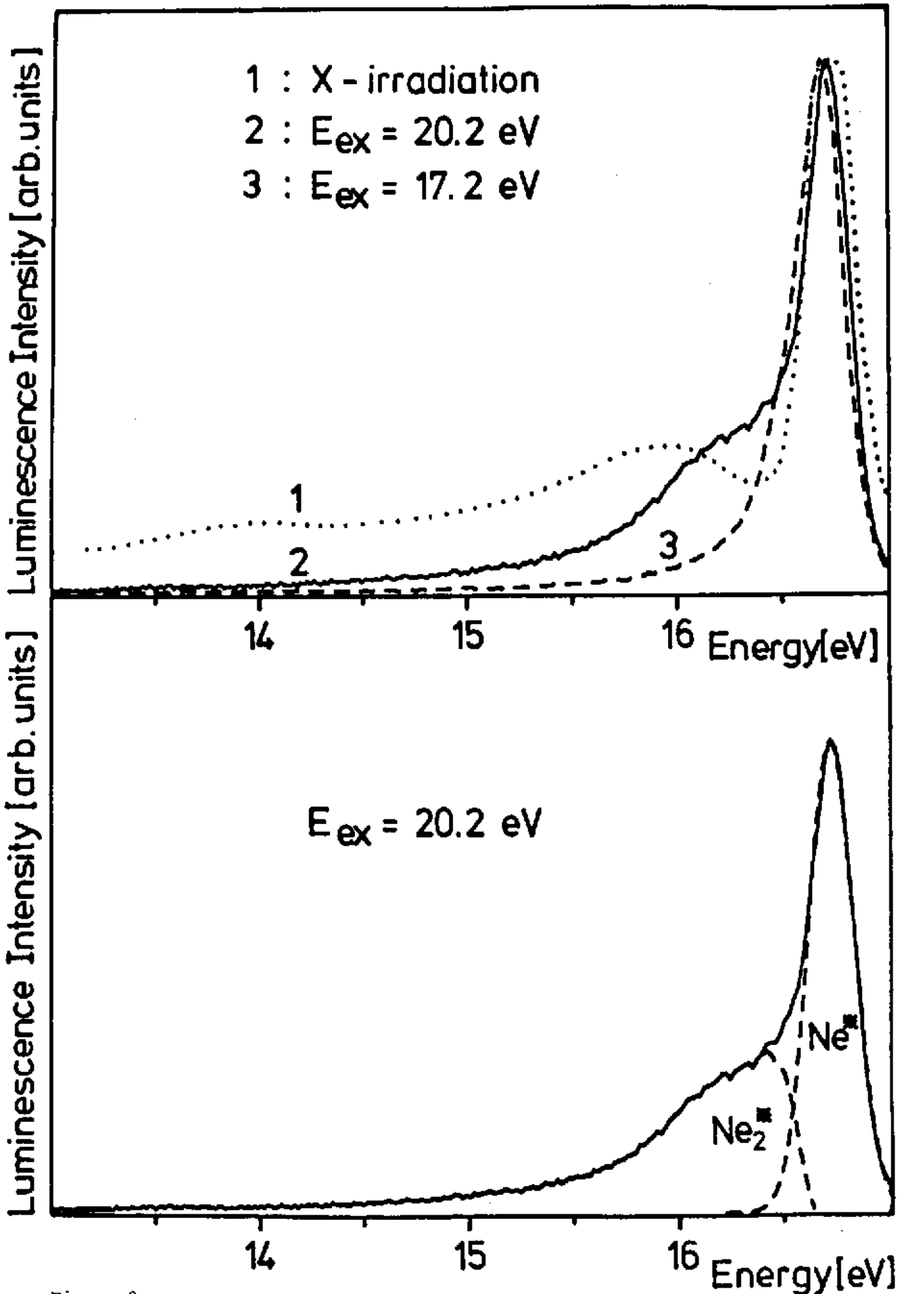

Figure 3

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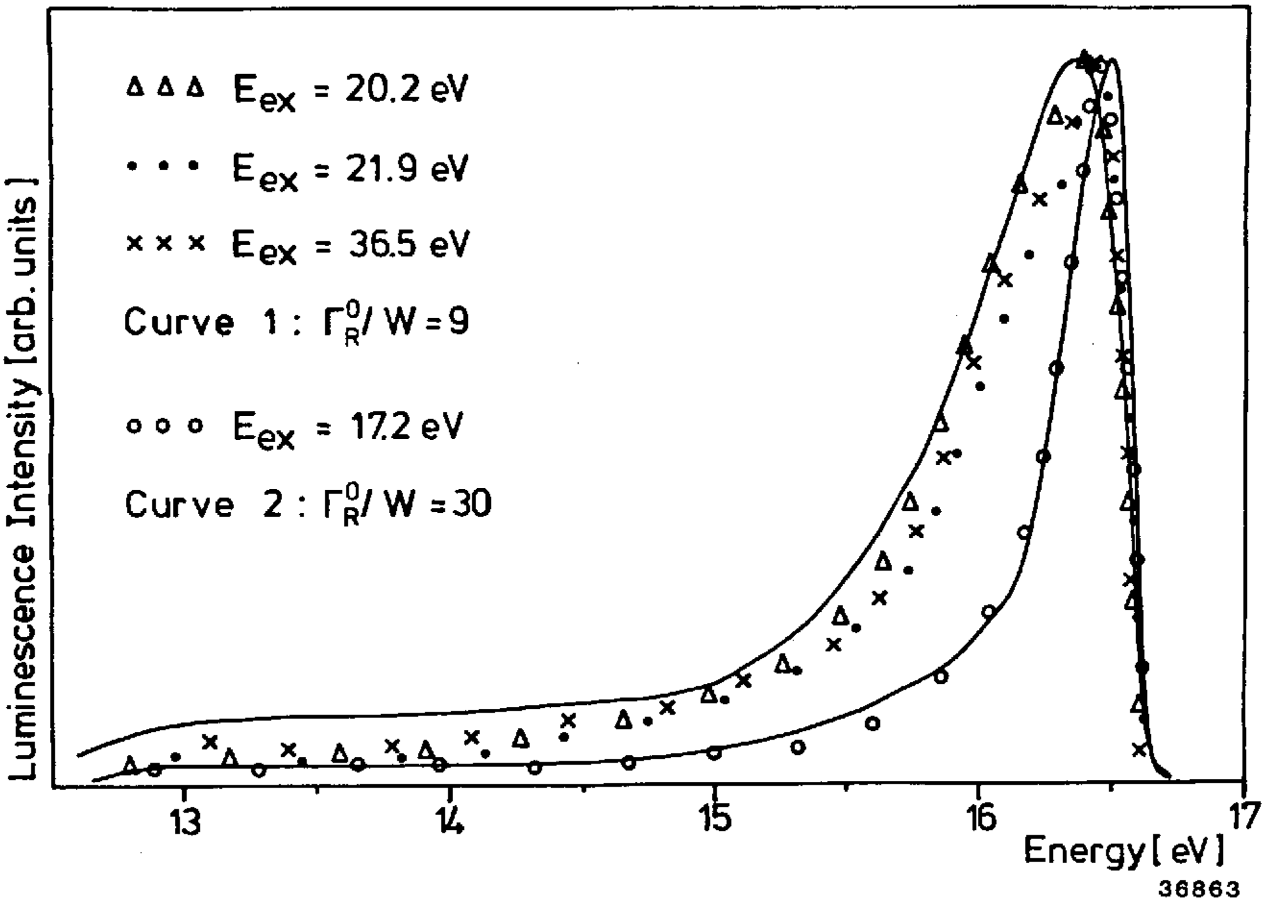

Figure 4

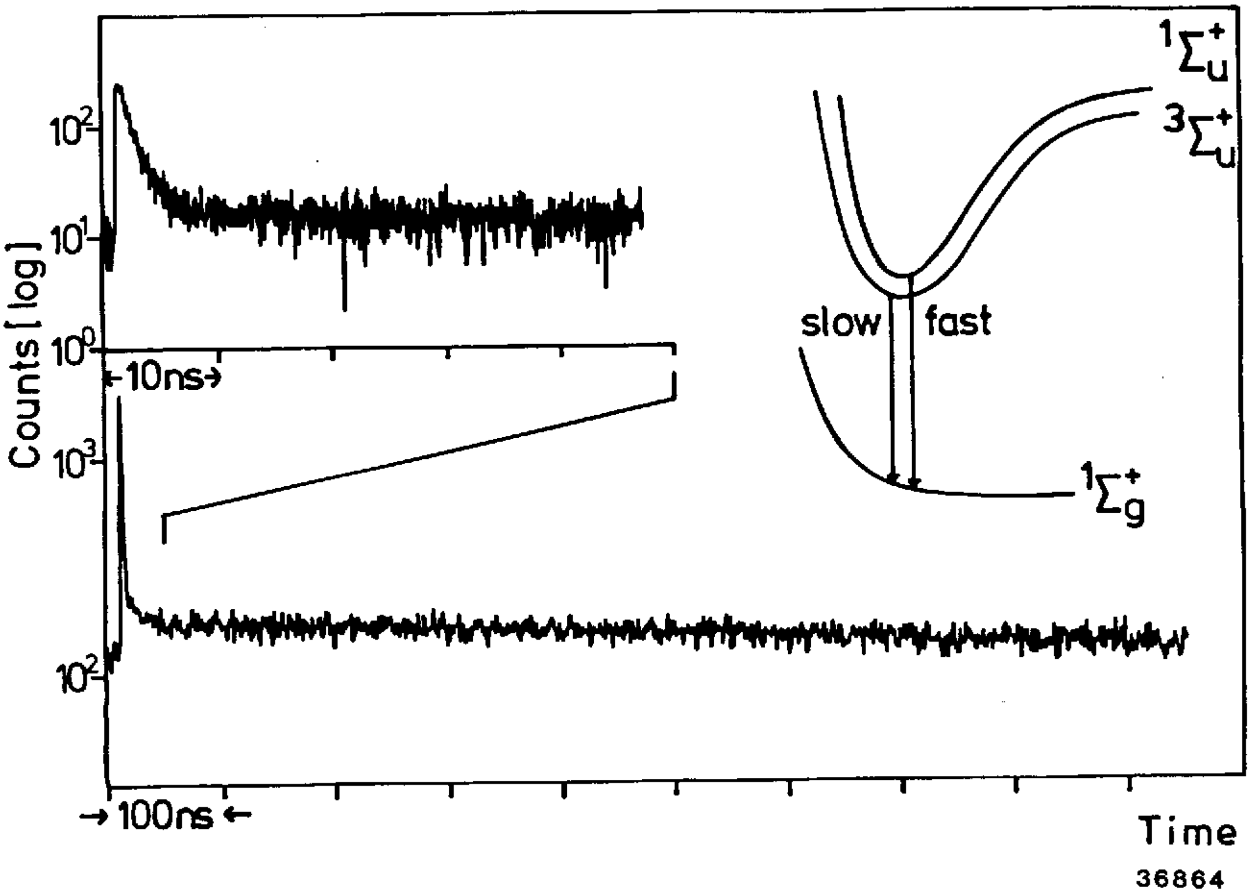

Figure 5