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Self-Trapping of Hot and Thermalized Excitons in Solid Xenon

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The first direct measurement of the self-trapping rate, Γ_{ST}, of thermalized excitons in solid Xe is presented. The temperature dependence of Γ_{ST} is explained by thermal assisted tunneling through the self-trapping barrier separating free and self-trapped exciton states. The results agree with recent theories on self-trapping. The ratio of luminescence intensity of free and self-trapped states disagrees with the measured self-trapping rates and displays the role of self-trapping of hot excitons.

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1. INTRODUCTION

The coexistence of free and self-trapped exciton states as a consequence of exciton phonon interaction in a deformable lattice was the subject of recent experimental[1,2] and theoretical[3-5] investigations. It was established in luminescence experiments in alkali halides[1] and rare gas solids[2] which clearly yield luminescence of free excitons and broad band, Stokes-shifted emission of self-trapped excitons.

The coexistence is due to the fact that the adiabatic potential surface of the exciton interacting with the lattice has two minima. One minimum represents the exciton state in the undeformed lattice, the so-called "free exciton", FE. In the mentioned materials it is metastable. The other minimum represents an exciton accompanied by a local lattice deformation (atomic displacements), the so-called "self-trapped exciton", STE. Both states are separated by a potential barrier (self-trapping barrier). If we represent the lattice deformation by a single configuration coordinate, Q, we get the potential diagram shown in Fig. 1. It explains the qualitative behaviour of luminescence. As an example, a typical luminescence spectrum of solid Xe is included with its FE contribution at ∿8.3 eV and its STE contribution centered at ∿ 7.1 eV.

Self-trapping of excitons is usually ascribed to tunneling through the barrier (low temperatures; path (1) in Fig. 1, tunneling probability Γ_o) and to thermal activation (higher temperatures; path (2), probability $\propto \exp(-W/kT)$). In this paper it is shown that we have to distinguish between self-trapping of hot excitons and of thermalized excitons. For hot excitons, the self-trapping barrier is practically transparent. Thermalized excitons are self-trapped via thermal assisted tunneling (path (3) in Fig. 1).

The self-trapping probability, Γ_{ST}, of thermalized excitons reflects the detailed nature of exciton phonon interaction. For rare gas solids (RGS) only deformation potential interaction with acoustic phonons has to be taken into account[2]. RGS thus play the role of model substances for self-trapping of excitons. This paper presents the first direct measurement of Γ_{ST} of a RGS. Xe shows the most prominent FE luminescence of all RGS. It is thus the most promising candidate for the experiment.

The first theoretical estimate of Γ_{ST} in RGS yielded $\Gamma_{ST} \gtrsim 1.7 \times 10^{11} s^{-1}$ [6]. Especially for solid Xe, Γ_{ST} was also estimated from the relative intensities of FE and STE luminescence according to $I_{FE}/I_{STE} = \Gamma_R/\Gamma_{ST}$ (Γ_R: radiative decay probability of FE). Values of $\sim 5 \times 10^{10} s^{-1}$ [7] and $\sim 10^{12} s^{-1}$ [2] were obtained.

More rigorous calculations by Rashba (3) and Nasu and Toyozawa (5) indicated that Γ_{ST} might be considerably smaller. This encouraged us to measure the lifetime, τ, of FE luminescence in a conventional time resolved luminescence experiment.

2. EXPERIMENT

Our study was undertaken in the synchrotron radiation (SR) laboratory HASYLAB (Hamburg). SR from DORIS II consists of sharp light pulses (fwhm $\sim$ 150 ps) at a repetition rate of $\sim$ 1 MHz and is well suited as an excitation source for time resolution down to the $\sim$ 50 ps range [8]. The experimental set up [9] and the method of measurement are described elsewhere [10].

The measurements were performed under primary excitation of n = 2 exitons. The excitation energy was chosen as a compromise between two requirements. To avoid scattered light superimposed to luminescence it should be far off the luminescence energy. On the other hand, to avoid the influence of hole - electron recombination processes on the time evolution of luminescence, excitation in the excitonic region of absorption is indispensable.

The samples were condensed near the sublimation temperature at 55 - 60 K at a deposition rate of $\sim$ 2000 Å/min on a LiF substrate. The high deposition temperature is indispensable to get FE luminescence. To ensure purity of the samples, gas handling and sample chamber are ultrahigh vacuum systems. Xe of a nominal purity of 99.997 % was used. The purity was checked with a mass spectrometer.

3. RESULTS AND DISCUSSION

Fig. 2 shows decay curves of FE luminescence at different temperatures. The lowest curve was measured with prompt stray light and thus yields the convolution of the shape of the excitation pulse, the detector response and electronics. It has a fwhm of $\sim$ 200 ps but a tail to longer times. The decay curves (1) to (4) contain luminescence light and some residual scattered light (both monochromators of the set up are only single pass instruments). The lifetimes given in Fig. 2 were obtained from numerical evaluation including deconvolution with the apparatus function.

The self-trapping rate Γ_{ST} is obtained from the decay rate $\Gamma = 1/\tau$ via $\Gamma_{ST} = \Gamma - R_R$. Γ_R itself is not known. We take $\Gamma_R \approx 2 \cdot 10^8 s^{-1}$ (approximately the decay rate of gas phase Xe $^3P_1$ atoms [11]). The estimate influences the conclusions only marginally because $\Gamma_{ST} >> \Gamma_R$.

In Fig. 3, Γ_{ST} is plotted as a function of temperature (lower curve). Evidently, Γ_{ST} has a strong temperature dependence even at rather low temperatures. The ratio, Γ_R/Γ_{ST}, therefore sharply decreases (Γ_R: independent of T) with increasing T. This is in striking contrast to the temperature dependence of the intensity ratio, I_{FE}/I_{STE}. A typical measurement of the intensity ratio is included in Fig. 3 (see also Ref. 12). A striking difference is also found for the values of Γ_R/Γ_{ST} and I_{FE}/I_{STE} at low T. The ratio of the probabilities is $\sim$.1 whereas the intensity ratio is $\lesssim$.01 (this paper) to $\sim 10^{-3}$ [12]. It is obvious that we are not allowed to identify Γ_R/Γ_{ST} with I_{FE}/I_{STE} as was done before. In other words, those excitons which show up in the FE luminescence line are not the precursors of the majority of self-trapped excitons.

This surprising result is supported by an analysis of the rise of STE luminescence which does not display the decay of FE luminescence but which is prompt (as fast as stray light). This was measured for different excitation energies and different temperatures [13].

Obviously, under primary excitation of higher members of the exciton series, in the course of electronic relaxation, excitons are self-trapped before they reach thermal equilibrium. For hot excitons with an average kinetic energy comparable to the height, W, of the barrier ($\sim$ 20 meV for Xe, see below) the self-trapping barrier is practically transparent. Thus I_{FE}/I_{STE} is mainly

determined by the branching between thermalization and self-trapping of hot excitons. This conclusion is supported by an estimate of this branching. Self-trapping of hot excitons cannot be faster than $\sim \omega_D$ (Debye frequency), $\sim 8 \cdot 10^{12} s^{-1}$. The phonon scattering rate Γ_{ph} of excitons approaching the minimum of the exciton band is of the order of $10^{10} \ldots 10^{11} s^{-1}$ [14]. The ratio $\Gamma_{ph}/\omega_D \approx 10^{-2} \ldots 10^{-3}$ is in qualitative agreement with I_{FE}/I_{STE}. As Γ_{ph} is expected to increase with increasing temperature, even an increasing I_{FE}/I_{STE} can be rationalized. The drop of I_{FE}/I_{STE} around 55 K is explained below.

The measured self-trapping rate Γ_{ST} displays the dynamical behaviour only of that small fraction of excitons which are scattered to states for which the self-trapping barrier is effective. Then they have a chance to thermalize. The conclusions drawn from Γ_{ST} as a function of T concern only these excitons. To explain the measured data we first assumed a superposition of tunneling (path(1)) and thermal activation (path (2) in Fig. 1), $\Gamma_{ST} = \Gamma_o + a \exp(-W/kT)$. A satisfactory fit of the measured data with this expression was not possible.

Much better agreement was obtained with Rashba's theory of self-trapping via thermal assisted tunneling [3,15]. It predicts

$$\Gamma_{ST} = \Gamma_o \cdot \frac{1}{(1-T/\theta)^{\alpha}} \qquad (\text{for } T \ll \theta) \qquad (1)$$

θ: Debye temperature, α is an exponent of the order of 2...3 and contains information about the actual density of states of the exciton band. The full curve in Fig. 3 is a fit of the measured points with Rashba's expression. The agreement is obvious. From the fit we get $\Gamma_o = 1{,}3 \cdot 10^9 s^{-1}$ and $\alpha = 2{,}56$. The value of Γ_o has to be regarded as an upper limit because quenching effects are ignored in our consideration. Moreover, Γ_o may also be influenced by imperfection of the samples.

Though equ.(1) is only valid for $T \ll \theta$ it can be assumed that thermal assisted tunneling drastically increases Γ_{ST} at higher temperatures. The drop of the intensity ratio around 55 K is therefore ascribed to thermal assisted tunneling at a temperature at which the barrier is practically transparent even for thermalized excitons.

Rashba has given an analytical expression which relates Γ_o to other quantities (3,15)

$$\Gamma_o = \omega_D \exp\left\{ -5{,}6 \cdot \frac{\rho s^2}{m^2 C^2} \right\} \qquad (\hbar = 1) \qquad (2)$$

ρ : density, s: velocity of sound, m: exciton mass, C: deformation potential. A numerical calculation of Γ_o from equ.(2) is impeded because some of the quantities are not known well enough. Moreover, Rashba indicates that a refined treatment decreases the numerical factor in the exponent [15]. In spite of this we calculated the less well known quantities, m·C, from $\Gamma_o = 1{,}3 \cdot 10^9 s^{-1}$ and equ.(2), $m \cdot C \approx 10\ m_e \cdot eV$ (m_e: free electron mass).(ρ and s were taken from ref. 2). This is somewhat larger than what we obtain with $C \approx 1 \ldots 2$ eV and $m \approx 2 \ldots 3\ m_e$ [2].

Γ_o has also been calculated by Nasu and Toyozawa [5] who combined the theory of multiphonon nonradiative transitions and the variational method for the tunnel path. In their paper, Γ_o is not given analytically but graphically as a function of the halfwidth, B, of the exciton band, and the deformation type dimensionless coupling coefficient, S_l, from which only the order of magnitude is known [5]. So, it is not possible to compare directly theory and experiment. However, from our measured Γ_o, in connection with Fig. 8 of ref. 5, $S_l^2/2 = 140$ is obtained (hereby B = 0,45 eV, $\hbar\omega_D$ = 5,5 meV [2] were used). Then, from Fig. 3 of ref. 5, the height of the self-trapping barrier is determined, $W \approx 5\ \hbar\omega_D \approx 25$ meV. Note, this value is determined from a tunneling rate. It is in quite good agreement with $W \approx 20$ meV deduced by Fugol [2] from the Stokes shift between FE and STE luminescence. Therefore, theory of Ref. 5, the conclusion based on the measurement of relaxation energy [2] and our results concerning the tunneling rate Γ_o are consistent with each other.

Acknowledgement

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Figure Captions

Fig. 1 Energy, E, of the exciton interacting with the lattice, as a function of a configuration coordinate, Q. Q_o is the value of Q in the unrelaxed lattice. The origin of FE and STE luminescence is indicated by arrows. Lower curve: luminescence spectrum of solid Xe at T = 8 K under photon excitation at 9.1 eV.

Fig. 2 Typical decay curves of FE luminescence of solid Xe at different temperatures. Temperatures and lifetimes are given in the figure. For comparison, time evolution of scattered light is included.

Fig. 3 Self-trapping rates of (thermalized) excitons in solid Xe as a function of temperature. Full curve: Rashba's theory. Dashed curve: intensity ratio I_{FE}/I_{STE} as a function of temperature (excitation energy 9.1 eV).

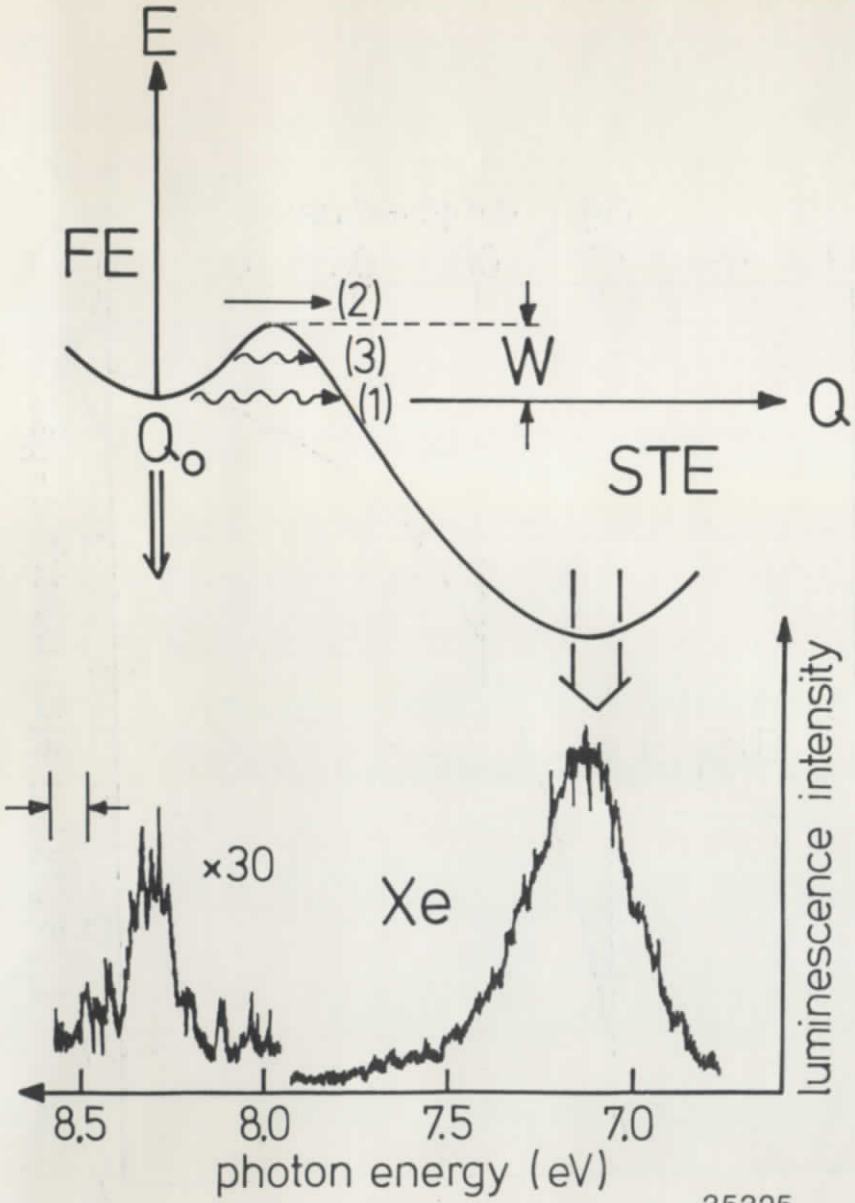
E
FE
(2)
(3)
(1)
W
Q
Q_o
STE
×30
Xe
luminescence intensity
8.5
8.0
7.5
7.0
photon energy (eV)
35325

FIG. 1

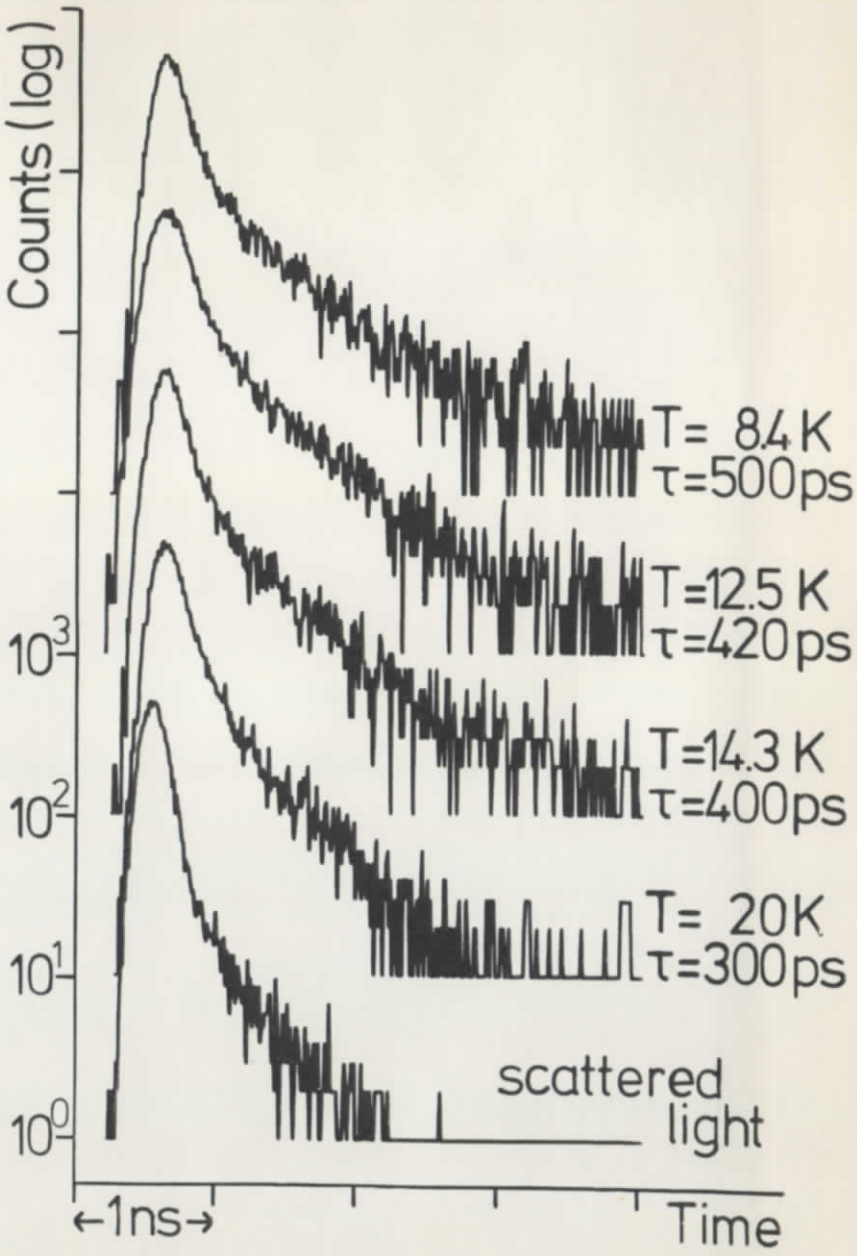
Counts (log)
10^3
10^2
10^1
10^0
T= 8.4 K
τ=500ps
T=12.5 K
τ=420ps
T=14.3 K
τ=400ps
T= 20K
τ=300ps
scattered
light
←1ns→
Time
35323

FIG. 2

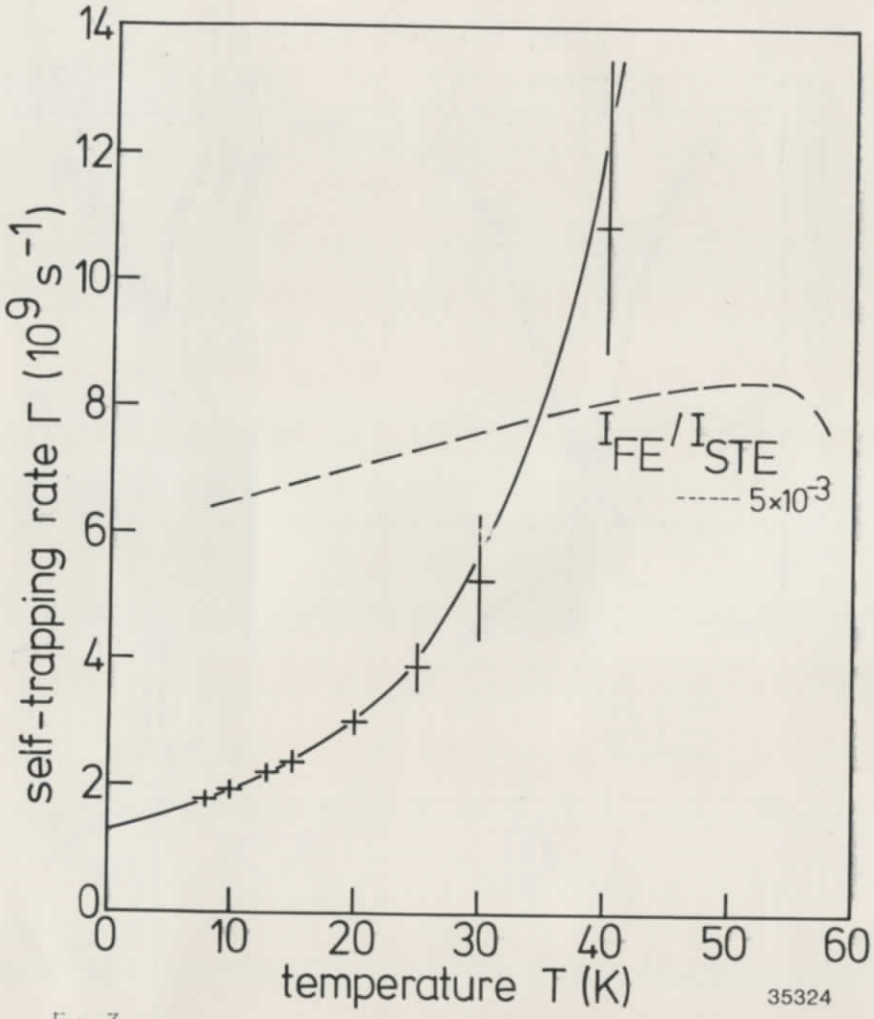
14
12
10
8
6
4
2
0
0
10
20
30
40
50
60
self-trapping rate Γ (10^9 s^{-1})
temperature T (K)
I_{FE}/I_{STE}
----- 5×10^{-3}
35324

FIG. 3