Time-resolved resonance Raman scattering and luminescence from confined excitons in AgBr quantum dots

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Abstract: Resonantly excited low temperature Raman scattering and luminescence are investigated in AgBr microcrystals produced in reversed micelles. The crystallite size is close to the exciton Bohr radius in the bulk resulting in a blue shift of the luminescence. Under excitation resonant with the exciton one and two phonon Raman scattering is observed involving TO(L), LO(Γ) and odd parity L-phonons, respectively. The temporal behaviour of these processes after pulsed excitation reflects the decay of the confined exciton states. The lifetime is found of the order of 500 μ s and mostly determined by radiative decay.

1 Introduction

Quantum size effects of excitons in spatially confined structures are of interest both with regard to testing fundamental solid state concepts and to applications related to the optical nonlinearities (for references see e.g. [1–4]). A variety of semiconductor materials, like CdS, CdSe and cuprous halides, was produced as three-dimensionally confined microcrystals with nanometer size ("quantum dots") embedded in an insulating glass or alkali halide matrix. While all these materials have direct electronic band gaps and therefore short radiative decay times below 1 ns, it was only recently that size restriction effects in indirect gap materials such as Ge and AgBr were reported [5–8]. Here one may expect long radiative lifetimes, which due the increasing admixture of Γ point band states, by non-conservation of wavevector in the small crystallites, are strongly size dependent [9].

AgBr is known to have the lowest exciton state at point L in the Brillouin zone. Therefore in the bulk, this gives rise to phonon assisted absorption and emission processes with allowed transitions involving a TO(L) and LA(L) phonon, respectively, and weaker forbidden TA(L) and LO(L) assisted transitions giving rise to characteristic two-phonon resonance Raman scattering (see e.g. [10]). In the small particles the observed confinement effect leads to a blue shift of the emission which is accompanied by a strong enhancement of intensity. In addition, we recently observed strong TO(L) and LO(Γ) one-phonon Raman scattering in resonance with the confined exciton states. These processes involve a no-phonon optical transition to the indirect exciton states. As is well known

from other time-resolved light scattering studies, the temporal behaviour of these processes directly reflects the phase and energy relaxation processes of the confined exciton states [11].

In this paper we report first measurements of time-resolved resonantly excited Raman scattering and luminescence in AgBr microcrystals with diameters comparable to the exciton Bohr radius. Our results demonstrate that the exciton states in these crystallites have lifetimes of the order of 500 μ s mostly determined by radiative decay.

2 Experimental

The small AgBr particles were prepared by employing the method of reversed micelles essentially following the procedure described by Johansson et al. [6]. The components to start with were separate water solutions of KBr and AgNO₃. These were added to AOT (dioctyl sulfo-succinate) that forms the micelles and was solved in a trimethylcyclohexane/water mixture. The solutions were poured into a special sample holder suitable for the optical measurements, briefly mixed to form the AgBr particles and immediately cooled down to liquid nitrogen temperatures. Precautions were undertaken to keep the material in the dark during all preparation until the low temperatures were reached. By choosing the molar ratio $\omega = [\text{H}_2\text{O}]/[\text{AOT}] = 10$ average diameters of the AgBr particles around 6 – 7 nm were achieved, as concluded from the analysis of the exciton transitions [8].

To take the time-resolved spectra two different setups were employed. In the first, we used a dye laser operating with Stilbene 3 and synchronously pumped by the third harmonic of a Nd:YLF laser system to produce 5 ps laser pulses. The emitted light was dispersed with a double monochromator and detected by a photomultiplier tube employing single photon counting (time-resolution 30 ps [11]). The longer decay times were measured with the second setup employing a chopped cw laser and a boxcar detection system (frequency 125 Hz, maximum time-resolution 200 ns).

3 Results and Discussion

Fig. 1 displays the low temperature time-integrated luminescence spectrum of a typical sample excited at a photon energy $E_L = 2.93$ eV. It shows two main emission bands which we ascribe to size-quantized free exciton states (FE) and to donor-acceptor type transitions (D-A) similar to those in bulk material. Only a faint broad structure occurs at around 2.5 eV possibly reminiscent of the well-known iodine bound exciton [12] which is strongly suppressed due to the impurity exclusion effect [6, 7]. The FE peak at 2.73 eV corresponds to a confinement-induced energy shift of about 50 meV. This is much larger than the free indirect exciton binding energy in bulk material ($E_{bx} \simeq 32$ meV [10]) demonstrating intermediate to strong confinement [1]. The width of the band ($\simeq 50$ meV), besides being due to the superposition of different transitions, is largely inhomogeneous and caused by the distribution in particle size.

The time dependence of the FE emission under similar excitation conditions is shown in Fig. 2. It consists of two components with lifetimes of 2.5 ns and 550 μ s. Time-gated measurements of the luminescence spectra (not shown) reveal that the slow component is due to the FE states while the

Fig. 1 Luminescence spectrum of a typical AgBr microcrystal sample showing free exciton (FE) and donor-acceptor type emission (D-A). Excitation photon energy $E_L = 2.93$ eV. $T = 5$ K. R denotes a Raman line of the solvent, the arrow indicates the exciton band gap energy of bulk AgBr.

Fig. 2 Time-dependence of the FE emission detected at $E_S = 2.73$ eV after chopped excitation at $E_L = 2.90$ eV. Zero of time scale: switching-off time. Inset: time-dependence of FE emission in a linear intensity scale after picosecond pulsed excitation at $E_L = 2.90$ eV. $T = 5$ K.

short time must be attributed to states extending from the D-A band to higher energies. A similar short decay was previously observed for excitation at much higher photon energy [6]. Different from the non-exponential decay kinetics found for confined direct excitons [2, 3], in AgBr the FE shows a single exponential time behaviour over two orders of magnitude. Moreover, the lifetime is much longer than that found in typical bulk samples, where it is of the order of several nanoseconds and determined by non-radiative decay processes. It rather corresponds to the expected bulk radiative lifetime of some milliseconds [10] proving that in the small particles radiative recombination dominates the FE decay. This is completely confirmed by the time behaviour of the one and two phonon Raman lines occurring under resonant excitation (Fig. 3). For fixed E_L , these correspond to the resonance fluorescence of excitons in quantum dots of definite size [8] and also show the expected long decay time.

The size dependence of radiative decay originates from the admixture of Γ point to L point valence band states. Using first order perturbation theory, the radiative recombination probability is given by [7]

$$\Gamma_{rad} = \Gamma_0 (1 + \alpha/(k_L R)^2) . \quad (1)$$

with Γ_0 the radiative transition probability of the indirect exciton in the bulk, k_L the L point wavevector and R the particle radius. The proportionality constant α determines the strength of the no-phonon transition for exciton wavefunctions of the size of a unit cell. To compare this formula with the measured exciton lifetimes at different confinement energies (see inset in Fig. 3), we have calculated the corresponding particle size as described in [8]. The full line shows the result obtained with $\alpha = 850$ and $\Gamma_0 = 1$ ms. Extrapolation of eq. (1) to an exciton size of a unit cell gives a radiative decay time of about 25 μ s, which compares well with the lifetime of an exciton bound to the iodine impurity [12], the wavefunction of which also extends over a similar volume.

Fig. 3 Time-gated spectra in a Raman-like plot (intensity versus Raman shift) under chopped laser excitation at different photon energies E_L showing the long lived spectral components. Time window from 50 μ s to 500 μ s after excitation switch-off. NP: position of no-phonon band of the $1s1s$ transition [8]. The horizontal lines mark zero of intensity for each spectrum. Inset: Dependence of exciton lifetime τ on the transition energy. Points: experiment; full line: calculated from eq. (1) (see text).

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