Direct Evidence for a Bottleneck of Exciton-Polariton Relaxation in CdS

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We provide direct experimental evidence for the existence of a relaxation "bottleneck" on the lower branch of the exciton-polariton dispersion curve in CdS. The exciton lifetime shows a distinct maximum of about 2.5 nsec in this energy range, as measured by time-resolved luminescence after excitation with a short, weak light pulse. There is no thermalization within the bottleneck region at 1.6 K.

A bottleneck region of accumulating relaxing exciton polaritons on the lower polariton branch has been postulated by Toyozawa.[1] We present the first direct results showing that in CdS this bottleneck is indeed observable through an increase in the time spent in this energy range by the transverse $A_T(\Gamma_5)$ exciton. Cadmium sulfide is chosen for these experiments because a great amount of literature exists for its excitonic optical properties.[2-5]

High-quality crystals have been used by selecting platelets with flat excitation spectra of exciton lines.[5-7] Time-resolved spectra were obtained with excitation from a mode-locked argon laser providing pulses of 200 psec at 4579 Å. Instrumental time resolution was 0.75 nsec, limited by the delayed-coincidence photon-counting technique.[8] Final resolution of about 0.2 nsec was possible by deconvolution of the signal.

Our measurements consisted of two parts. First we had to establish which luminescence is due to recombination from the transverse $A_T(\Gamma_5)$ exciton and then to investigate its kinetics.

Recently, Gross *et al.*[9] attributed two emission maxima in $E \perp c$ polarization to this exciton. Peak I (see curve *a* in Fig. 1), dominating at 1.6 K, lies at about 4857 Å (2.5520 eV)[10] and was suggested to originate from the knee of the lower polariton branch; peak II at about 4853 Å (2.5541 eV) was connected with the maximum of crystal-to-vacuum boundary transparence for polaritons.[9] We found three results confirming this assignment:

(i) The excitation spectra (ES) of *both* emission peaks I and II show sharp isolated maxima in compensated crystals (Fig. 2). These maxima are separated by the energy of one LO phonon.[5-7] In contrast, we find more complex structure in all ES of emission lines definitely connected with bound excitons and impurities.[6,7] High-energy tails of the former sharp excitation maxima would result from relaxation via acoustical phonon generation at the end of the LO phonon cascade.[5] Our ES of peak I show very little of such tails [Fig. 2(b)]. This indicates that peak I originates from the actual bottleneck region, where interaction with acoustic phonons is weak.[1] We find pronounced tails in the ES of the high-energy

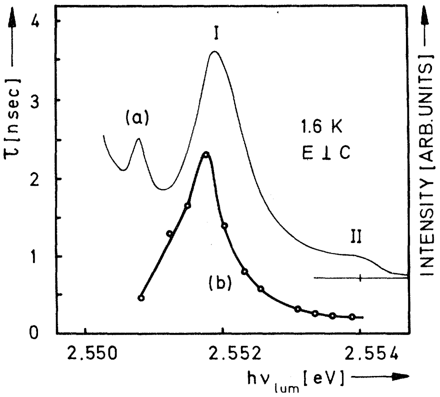

FIG. 1. Curve *a*, typical luminescence spectrum of a high-quality CdS platelet (right scale). Curve *b*, luminescence decay times at different energies (left scale).

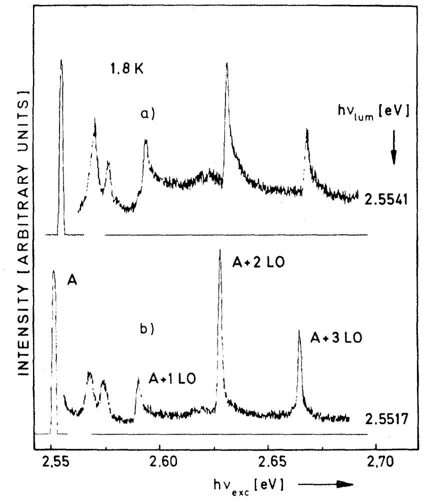

FIG. 2. Excitation spectra (a) of emission peak II and (b) of emission peak I. The width of the direct scattering line *A* corresponds to our spectral resolution.

emission II [Fig. 2(a)], where interaction with acoustic phonons is more effective.

(ii) We can shift the position $h\nu_{\rm lum}$ of peak I throughout the bottleneck region in linear correspondence to the variation of the excitation energy $h\nu_{\rm exc}$ for crystals with pronounced excitation spectra. All other lines connected with impurities *and* peak II remain fixed in these measurements. The shifting peak I just occurs at an energy where the exciton has arrived after relaxation by LO phonon emission.

(iii) We compared our measured lifetimes of bound excitons in high-quality crystals with recent results of Henry and Nassau.[11] In addition to their results of roughly 0.5 and 1.0 nsec for the I_2 and I_1 lines, respectively, our analysis also yields a trapping time of about 2.3 nsec. This is the lifetime of the free excitons to be trapped. The only emission band having 2.3-nsec lifetime is line I at 2.5520 eV, which is thus proved to be due to free excitons. In crystals of lower quality this lifetime shortens considerably and, consistent with this, the trapping times for the I_2 and I_1 bound excitons also shorten. Their lifetimes, however, remain fixed.

After having clarifed which emission is due to the free A exciton, we now come to the main result concerning the kinetics. Curve b in Fig. 1 shows the luminescence-decay times of exciton emission for high-quality crystals. These times strongly depend on the emission energy $h\nu_{\rm lum}$. The longest time of about 2.3 nsec is measured near the low-energy emission maximum I. In Fig. 3 we present a simple schematic for qualitative description of this result.[12] The bottleneck region is divided into three ranges a, b, and c. The decay times of luminescence in each range are determined by three time constants: the relaxation time from one range to the next lower range in energy, the radiative lifetimes, and the nonradiative lifetimes. The latter are supposed to be energy independent. The transition probabilities per particle are symbolized for the three channels by arrows of different thickness. In high-quality crystals with flat ES all three ranges are filled about equally with excitons shortly after the excitation pulse by direct relaxation of continuum excitations (dotted arrows).[7] Relaxation from a to b is rather fast and the radiative lifetime in a is short because of the minimum in reflectivity R.[1,9] Both these times determine the short decay constants of $\lesssim 0.2$ nsec at high energies. Relaxation from b to c is slow and excitons pile up in range b. Despite the comparatively long radiative lifetime in this range of maximum R we therefore get the emission maximum I. In c the radiative lifetime decreases again as does the observed decay time τ and the emission intensity.[13] These facts demonstrate that relaxation from b to c by acoustical phonon generation is slow and only few excitons come from b to c within the 2.3-nsec lifetime in range b. The initial population in c is achieved by direct relaxation from continuum electron-hole pair excitations.[7] This is confirmed by the short rise time found for the luminescence signal from range c. Lower-quality crystals have much shorter lifetimes due to nonradiative recombination. Except for a less-pronounced maximum near peak I they are often shorter than our resolution of about 0.2 nsec.

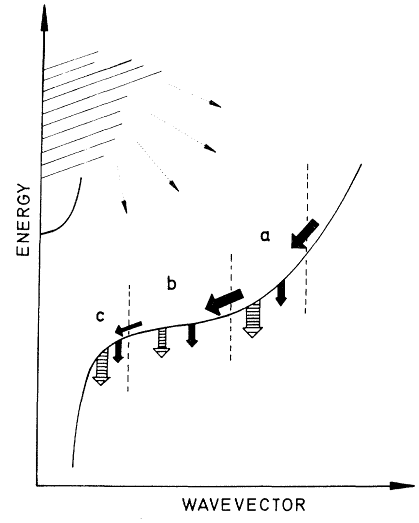

FIG. 3. Schematic diagram of the relaxation processes of high-quality crystals in the bottleneck region of the exciton-polariton dispersion curve. The shaded region symbolizes the exciton and free-electron–hole pair continuum. Dotted arrows, initial relaxation of continuum excitations into the bottleneck region. Solid arrows, nonradiative processes; striped arrows, radiative processes. The widths of these arrows represent the probabilities of the different processes.

The wavelength-dependent lifetime in the bottleneck region of the exciton polariton not only gives direct evidence for a pileup of excitons at the knee of the dispersion curve, it also demonstrates that no thermal equilibrium between excitons is achieved at 1.6 K even in pure crystals. The energy range over which luminescence is observed is larger than 2 meV. This large range cannot be thermally populated by excitons of 1.6 K. However, even a thermal distribution of excitons with higher temperature than the lattice can be ruled out. An equilibrium distribution with some defined temperature would lead to an effective experimental decay time which is equal at all emission energies. In addition, we observe sharp structure even in the ES of medium- and high-quality crystals, though it is situated on a large background. Such sharp structure would be smeared out in equilibrium.[7] We conclude that the flat excitation spectra in pure crystals are not due to thermal equilibrium as postulated by Gross *et al.*[5] They may be connected with the dominant continuum absorption as explained by Planel, Bonnot, and Benoît á la Guillaume.[7] Several authors have analyzed the line shape of 1LO and 2LO phonon replicas of the *A* exciton and could approach them with a Maxwell distribution of excitons.[14] However, this was always done at higher temperature and/or at much higher excitation densities than we have used.

In conclusion, we have shown that our decay-time data at 1.6 K give evidence for the existence of a bottleneck region for relaxation which is occupied by a polariton distribution not in thermal equilibrium. The relaxation times of the excitons via acoustic phonon scattering in this bottleneck region are found to be in the nanosecond range.

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[12] A more detailed model should take into account surface recombination, which in connection with long diffusion lengths and a wavelength-dependent absorption coefficient might simulate wavelength-dependent lifetimes [C. J. Hwang, J. Appl. Phys. 42, 4408 (1971)]. However, we find similar wavelength-dependent behavior of the decay times in the 1LO and 2LO replicas of the *A* exciton where absorption is negligible.

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Orientational Order Parameter in Solid CD_4

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Superlattice reflections below the I/II phase transition of solid heavy methane are connected with the orientational ordering that occurs. As a consequence of a temperature-dependent neutron measurement, they may be grouped into two classes, both with structure amplitudes following exponential laws but having different exponents $\beta = 0.21$ and $\beta' = 0.31$. This experimental behavior is well understood on the basis of a molecular-field-type analysis, which also shows that the system is close to a hypercritical point.

At 27.0 K, solid CD_4 undergoes a phase transition from its plastic high-temperature phase[1,2] (space group $Fm3m$) to the orientationally ordered phase II (space group $Fm3c$).[1,2] In the plastic phase the probability distribution of the D nuclei on a spherical shell around the C nucle-