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Dynamics of exciton-polariton recombination in CdS

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The dynamics of exciton-polariton recombination in CdS are investigated by measuring time-resolved luminescence spectra between 1.5 and 80 K. Decay times of free and bound excitons in $\vec{E} \perp \vec{c}$ and $\vec{E} \parallel \vec{c}$ polarization are determined for various types of crystals using low-excitation densities. The experiments prove the existence of a bottleneck for the relaxation and establish its location. Transverse excitons above the "knee" of the dispersion curve are found to be in thermal equilibrium with the lattice at temperatures higher than 30 K. At low lattice temperatures, excitons above the "knee" are in partial quasiequilibrium shortly after pulse excitation. The effective temperature of this exciton distribution exceeds that of the lattice and decreases rapidly within the observed exciton lifetime of 2.5–3 nsec.

I. INTRODUCTION

The direct-gap II-VI compound CdS is a widely used model substance for studies of the principal channels of electron-hole and exciton recombination. Free and bound states have been identified in absorption, reflection, and luminescence by Thomas and Hopfield[1] and others.[2,3] The dynamics of exciton relaxation[4-6] were studied as well as the influence of exciton-photon coupling—i.e., of the polariton—on the emission line shapes and the exciton distribution statistics.[6-9] Recently, the present authors reported on the first direct decay-time measurements on free excitons in CdS at 1.6 K.[10] These measurements have now been extended to temperatures ranging from 1.6 to 80 K; the results provide new information concerning the concept of an "exciton temperature" at low excitation densities.

A major point in the discussion of emission line shapes of free exciton polaritons concerns the distribution function of excitons. Theoretical line-shape calculations are usually based on the assumption of thermal equilibrium or of a quasi-equilibrium.[3,6,9,11-13] However, it is not obvious that equilibrium can be established in a system having no well-defined low-energy limit to its density of states.[14] Such is the case for the exciton polariton, because the parabolic excitonlike portion of the dispersion curve merges into the light line (Fig. 1).[14] Toyozawa[15] suggested a bottleneck for exciton relaxation caused by a reduction of phonon scattering processes near the knee of the polariton dispersion curve.[15,16] With this assumption one expects an equilibrium distribution of excitons in the energy range well above the knee, provided the exciton lifetime τ_{ex} is sufficiently long. The results from our time-resolved luminescence measurements indeed confirm the existence of the expected bottleneck and establish its position. Our measurements further illustrate the wave-vector dependence of exciton-phonon scattering processes and give upper limits for exciton formation times in CdS.

II. EXPERIMENTAL

We investigated single-crystal platelets and crystal chunks of varying crystal purity. Some samples were annealed for 20 h at 600° C in vacuum to obtain compensated crystals.[17]

Time resolved spectra were obtained with excitation from a mode-locked argon laser providing pulses of 200-psec width in the 4579-Å line. The over-all instrumental time resolution was 0.75 nsec (width at half-height) as determined by the RCA 31000E photomultiplier and by the delayed-coincidence photon-counting technique.[18,19] The typical signal-to-noise ratios of our measurements allowed a final resolution of about 0.3 nsec by deconvolution of the measured signal.

The dependence of luminescence spectra on the excitation energy was measured with a setup consisting of two spectrometers: one for selection of the excitation energy from a 100-W high-pressure Hg lamp and one for detection of the luminescence. The two spectrometers were a 60-cm Jobin Yvon with 13-Å/mm dispersion and a 75-cm Double Spex with 10-Å/mm dispersion. A cooled RCA C31034 photomultiplier with three dark counts per second was used for detection of the signal.

The power of excitation was varied between 0.1 and 10 W/cm^2 for ordinary luminescence work, and between 3 and 300 W/cm^2 in the pulsed experiments. This choice gave the same average powers in both kinds of measurement. The excitation densities for the spectra in Fig. 3 were only 2×10^{-4} W/cm^2.

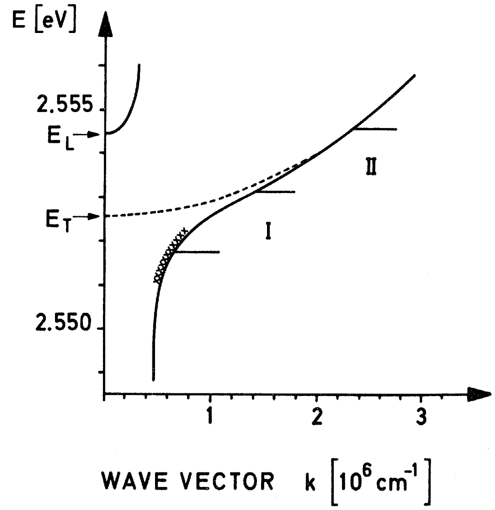

FIG. 1. Dispersion curve of the exciton polariton in CdS [full line, after Gross *et al.* (Ref. 8)]. The dashed line corresponds to the uncoupled transverse exciton. I and II are the two energy ranges of exciton emission at 1.6 K (see Fig. 2). The cross-hatched region indicates the approximate location of the bottleneck.

III. RESULTS

A. Luminescence spectra

Typical exciton emission spectra from high-quality platelets are shown in Fig. 2. The spectrum in Fig. 2(a) is obtained for polarization $\vec{E} \parallel \vec{C}$ at 1.6 K

The narrow line A_F ($\Delta E \leq 0.06$ meV) is due to the optically forbidden exciton having electron and hole spin parallel.[1] Line A_L is somewhat broader than A_F. A_L originates from the longitudinal exciton, which at $k=0$ is degenerate with the upper branch of the $A_T(\Gamma_5)$ exciton. The position of the A_L line can therefore be used as a measure for the onset of the upper polariton branch. The linewidth of A_L depends on the angle between the c axis of the crystal and the direction of observation,[6,7] which in our experiments was 90°.

The exciton emission with polarization $\vec{E} \perp \vec{C}$ is shown in Fig. 2(b), (c), and (d) for three temperatures. The energy scales of these curves have been shifted in order to compensate for the band-gap variation with temperature. The broad bands I and II have been identified by Gross *et al.* as emission from the transverse $A_T(\Gamma_5)$ free-exciton polariton.[8] This assignment is supported by our findings.[10] For further details on the emission spectra of CdS the reader is referred to the literature.[1-3,7]

Figure 3 shows the replicas involving the 1LO (lower-half) and 2LO (upper-half) phonon replicas of the free $A_T(\Gamma_5)$ exciton emission in a high-quality crystal for different excitation energies. Emission bands a, b and c had about equal intensity. The arrows in Fig. 3 indicate the energy position of the corresponding excitation line after subtraction of one or two LO phonon energies (37.9 meV), respectively. The LO replica emission shifts towards lower energy and decreases in linewidth when an excitation energy below the knee of the dispersion curve is chosen. The two and three curves, respectively, shown in Fig. 3 were selected for clarity from a series of curves with decreasing width and peak energy. The observed dependence of line shapes on excitation energy originates from direct excitation into (or slightly above) the bottleneck region of the exciton-polariton dispersion curve. For excitation above 2.556 eV, line shape and position of the phonon replicas do not depend on excitation energy. Such a dependence is observed only in crystals of lower quality.[10,20]

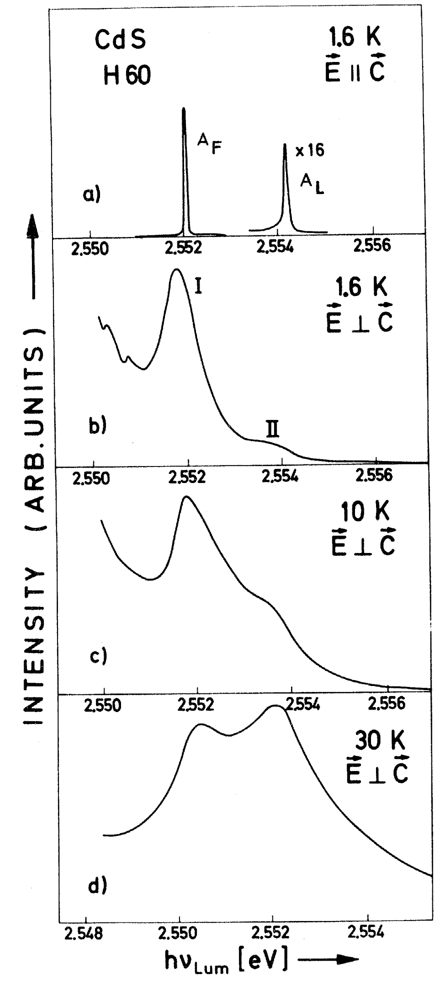

FIG. 2. Exciton emission spectra for various temperatures and polarizations.

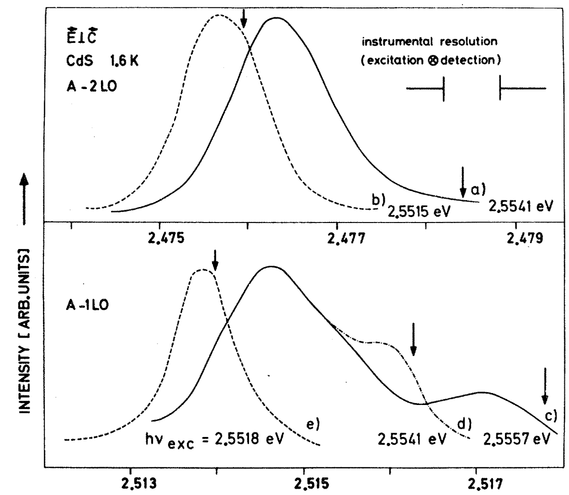

FIG. 3. Phonon replica bands of the A exciton emission for various excitation energies $h\nu_{\text{exc}}$. The arrows mark the energies $h\nu_{\text{exc}} - 2\hbar\omega_{\text{LO}}$ for curves (a) and (b), and $h\nu_{\text{exc}} - \hbar\omega_{\text{LO}}$ for curves (c), (d) and (e); $\omega_{\text{LO}} = 37.9$ meV. The excitation power was 2×10^{-4} W/cm^2. The given resolution results from a convolution of excitation linewidth and resolution of the analyzing spectrometer.

B. Decay times of free excitons

We have measured free-exciton decay times τ_{ex} at different temperatures and at various positions within the exciton emission band. The results are shown in Fig. 4 for a high-quality platelet. At 1.6 K a drastic dependence of decay time on emission energy is observed. In the high energy tail, τ_{ex} is below our resolution limit of about 0.3 nsec. τ_{ex} rises to a value of about 3 nsec slightly below the emission maximum at 2.5518 eV. In a preceding letter[10] we reported that τ_{ex} decreased again within the low-energy tail of the exciton emission band. After having analyzed a large number of crystals we found that this behavior is not universal. The reported decrease of τ_{ex} on the low-energy side seems to be due to the onset of superimposed emission from impurity-related recombination. Large exciton decay times are observed in the low-energy tail of the LO phonon replicas, where the impurity lines are less strongly replicated. The phonon replicas in general exhibited the same $\tau_{\text{ex}}(E)$ as observed in the zero phonon line.

It can be seen from Fig. 4, that the decay times in the high-energy tail of the exciton band increase with rising temperature. At 30 K τ_{ex} has approximately a constant value of 2.6 nsec at all emission energies. The highest temperature used in our experiments was 80 K. At this temperature the exciton decay is strongly nonexponential. It contains at least two decay times (1.5 and 7.5 nsec). At low temperature the observed exciton decay is not perfectly exponential either. However, the $1/e$ decay times given for τ_{ex} at low temperatures provide a reasonable description of the first decade of the decay.

The measured exciton decay times decrease with impaired crystal quality and in crystals of reduced quality are shorter than the final time resolution of our photon-counting technique. Measurements with the phase-shift method[19,21] at 1.6 K indicate that the energy dependence of these fast decay times on a relative scale is still similar to that observed in highest-quality crystals (Fig. 4). In parallel to reduced lifetime of excitons we observed more pronounced structure in the excitation spectra of crystals with impaired quality.[10] This observation agrees with the general ideas on the interdependence of lifetimes and excitation spectra.[4-6]

The decay time of the A_F line ($\vec{E}\parallel\vec{C}$) in crystals of high quality at 1.6 K has about the same value as has τ_{ex} at the maximum of the transverse exciton emission band, i.e., 2.5–3 nsec, but is longer than that of the transverse exciton at the energy of the A_F line. The A_L line, the $n=3$ and $n=2$ excited states of the transverse A exciton, and the $n=1$ state of the B exciton decay faster than 0.3 nsec. All data from the decay-time measurements are listed in Table I.

C. Decay times of bound excitons

We have also measured decay times of the bound exciton lines I_1 and I_2. The results from a typical

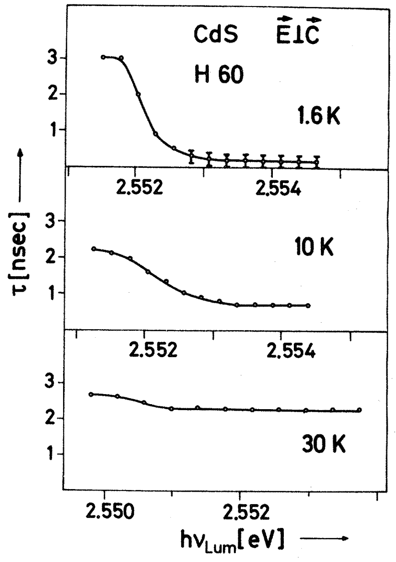

FIG. 4. Dependence of the exciton decay time $\tau_{\text{ex}}(E)$ on emission energy at three different temperatures.

TABLE I. Formation times τ_R and decay times τ_D of free and bound excitons in high-purity crystals.

Exciton-transition	$A_{n=3}$	$A_{n=2}$	$B_{n=1}$	$A_{n=1}$ band II	$A_{n=1}$ band I	A_L	A_F	I_2	I_1
Polariz.	$\vec{E}\perp\vec{C}$	$\vec{E}\perp\vec{C}$	$\vec{E}\perp\vec{C}$	$\vec{E}\perp\vec{C}$	$\vec{E}\perp\vec{C}$	$\vec{E}\parallel\vec{C}$	$\vec{E}\parallel\vec{C}$	$\vec{E}\perp\vec{C}$	$\vec{E}\perp\vec{C}$
τ_R (nsec)	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	2.5–3	2.5–3
τ_D (nsec)	< 0.3	< 0.3	< 0.3	< 0.3	2.5–3	< 0.3	2.5–3	0.6	1.0

high-quality crystal are summarized in Table I. The analysis of the data allows us to determine two time constants τ_R and τ_D for each line. In this analysis we assumed a time response of the luminescence proportional to $[\exp(-t/\tau_R) - \exp(-t/\tau_D)]$. τ_R describes the relaxation or trapping process and τ_D the decay time of the final excited state. By this analysis it is impossible to decide which of the two time constants belongs to the final recombination process. Our results for the I_1 and I_2 line are consistent with the data of Henry and Nassau[21] if we interpret the longer time constant of 2.5 nsec as the time τ_R of exciton supply to the complex and the 0.6 and 1 nsec as the bound exciton decay times τ_D of the I_2 and I_1 line, respectively. This is also a reasonable interpretation since the exciton supply time should be equal to the observed free-exciton lifetime τ_{ex}. Consistent with this view is the observation that τ_R in samples of lower quality decreases in parallel with the decrease of τ_{ex}, whereas τ_D keeps its high-purity crystal value.

Henry and Nassau[21] measured decay times by the indirect phase-shift method, which gives definite results only for strictly exponential decays.[19] They eliminated the effects of τ_R by direct excitation of the bound exciton in its acoustic phonon wing. We were not able to use this kind of excitation, which produced too much disturbing background radiation.

D. Time-resolved emission spectra of the A-2LO band

We have measured the A-2LO phonon replica of the transverse exciton emission at various times after pulse excitation. These satelite spectra reflect the polariton distribution essentially independent of surface effects because of the high transmissivity at such energies as compared with the zero phonon line.

The results are given by the open circles in Fig. 5. The times marking the three experimental curves are defined only within our direct resolution limit of 0.75 nsec. A deconvolution of the measured signal would have been rather difficult in this experiment. The limited time resolution somewhat blurs the true line shapes. However, the general trend is clearly observed: the emission bands decrease in width and shift to lower energy with increasing time after excitation.

IV. DISCUSSION

From the experiments we conclude that at temperatures above 30 K the polaritons are in thermal equilibrium with the lattice. At low temperatures such equilibrium with the lattice does not exist. Instead, the polariton distribution after weak-pulsed excitation is found to be time dependent. From that time dependence a region of low relaxation probabilities, the bottleneck region can be shown to exist.

Above the bottleneck region the polariton distribution can be described by a time-dependent effective temperature, which is higher than that of

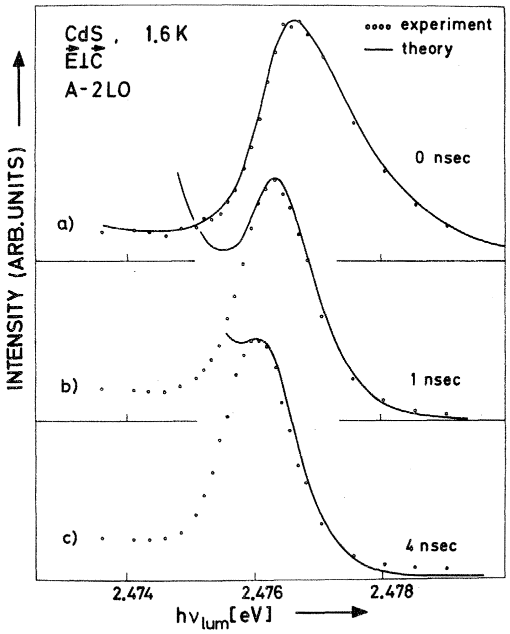

FIG. 5. Emission of the A-2LO replica band at three different times after pulse excitation. The theoretical fitting temperatures are (a) 10 K at 0 nsec (b) 5 K at 1 nsec, and (c) 4 K at 4 nsec after excitation.

the lattice. It is not clear, whether this indicates a real quasithermal equilibrium which would require rather efficient randomizing processes. Some estimates for characteristic times of the possible scattering mechanisms are made.

We will list our conclusions (in italics) and subsequently present our line of reasoning.

(1) *The excitons are in thermal equilibrium with the lattice at temperatures higher than 30* K. *Such equilibrium does not exist at 1.6* K. The observed exciton decay times should be identical at every point within the exciton emission band if the exciton population were in thermal equilibrium with the lattice. In this case the time dependence of the emission intensity $I(E,t)$ at some energy E is simply given by $I(E,t) \sim n_0(t)\, e^{-E/kT}$, where $n_0(t)$ is the time-dependent exciton population at an energy zero of the exciton system. It can be seen from Fig. 4 that $I(E,t)$ depends strongly on E at 1.6 K but is independent of E at 30 K. However, this does not rule out a relaxation process during which a time-dependent quasithermal equilibrium is established.

(2) *There is a bottleneck of exciton relaxation at the knee of the exciton-polariton dispersion curve. The scattering times in this energy range are several nanoseconds. Excitons within the bottleneck region do not reach an equilibrium which can be described by a temperature.* These conclusions can be derived from the data presented in Figs. 3 and 5. Figure 3 shows the position and width of the A-1LO and A-2LO replicas of high quality crystals to be influenced by the excitation energy. These changes can be achieved by choosing excitation energies near the knee of the dispersion curve. This process generates A-LO and A-2LO bands below the usual energy positions and of smaller widths. Emission from states at and below the knee is possible when the states are directly excited. There is little line broadening due to scattering and relaxation. It can be noticed from Fig. 3 that the A-2LO band excited in the knee region is considerably broader than the corresponding A-1LO line. This is probably due to participation of LO phonons from a wider range of the Brillouin zone.

Emission from states below the knee is not observed under usual conditions of nonresonant excitation. This is due to the slowness of the scattering processes which are necessary to populate these states. The scattering times can be concluded to be at least 3 nsec since excitons acculated above the knee after excitation at higher energies have a decay time of 3 nsec. The conclusion that scattering times for excitons into and between states at the knee are comparable or longer than the exciton lifetimes is also supported by the results given in Fig. 5, where line shapes of the A-2LO replica are given for different times after excitation. Obviously the exexciton population relaxes towards the knee region with increasing time after excitation. However, a thermal distribution within the states at the knee is not achieved.

The line shape of the A-2LO phonon replica can be analyzed to give the distribution function $f(E)$ of excitons within the polariton dispersion curve. We assume that in the relevant energy range the coupling of two LO phonons to the exciton is independent of the exciton wave vector k.[12,22] The line shape is then determined by the product of $f(E)$ and the density of states $N(E)$. From the experimental points in Fig. 5 we thus determined $f(E)$ at three different times after excitation. With the simplest assumption of a Boltzmann distribution for the excitons, the theoretical fit yields three different temperatures. The full lines in Fig. 5 have been calculated with $f(E) \sim e^{-E/kT}$ and using an approximate exciton-polariton density of states $N(E)$,[23]

$$
\begin{aligned}
N(E) &\sim K\left(\frac{d\Delta E}{dK^2}\right)^{-1} \\
&\approx K\{E_T^{-1}+1-(E_T^{-1}-1)\,[(E_T^{-1}-1)\,K^2-E_T]\}^{-1} \\
&\quad\times[\,(K^2E_T^{-1}-K^2-E_T)^2+8E_{LT}E_T]^{-1/2}\,,
\end{aligned}
\tag{1}
$$

with

$$
\begin{aligned}
K^2 &= \Delta E\,(1-E_T)+\tfrac{1}{2}E_T^2 \\
&\quad+\{[\,\Delta E(E_T-1)+\tfrac{1}{2}E_T^2]^2+2E_T^2E_{LT}\}^{1/2}.
\end{aligned}
\tag{2}
$$

$E_T = 2.5524$ eV is the energy of the uncoupled transverse exciton (Fig. 1), $E_{LT} = 2$ meV the longitudinal-transverse splitting of the exciton, $m^* = 1.3m_0$ the translational exciton mass,[22] and $\epsilon_0 = 7.8$ the background dielectric constant. ΔE stands for $E - E_T$. The energy E is measured in units of m^*c^2/ϵ_0, and the wave vector k in units of $m^*c/\hbar\sqrt{\epsilon_0}$. The fitting temperatures in Fig. 5 are 10, 5, and 4 K for curves (a), (b) and (c), respectively.

The calculated emission intensities rise steeply below the observed emission maxima (this rise depends on temperature and in curve a occurs below 2.474 eV). This rise is due to the nonvanishing density of states $N(E)$ of the exciton polariton below E_T and the assumption of thermal equilibrium. Below E_T the assumed exponetial distribution functions $f(E)$ increase more strongly than $N(E)$ decreases. Since the experimental curves do not show such an intensity rise at low energies we conclude that thermal equilibrium is not established in the knee region, the reason being low scattering rates and large group velocities. Excitons, once scattered into the knee region, can easily reach the surface before further scattering processes take place.[6] By the results derived from Figs. 3 and 5 the existence and position of a region with reduced exciton scattering is established. This region between 2.551 and 2.552 eV is the bottleneck postulated by Toyozawa.[15]

(3) *Excitons above the bottleneck assume a time-dependent distribution with effective temperature above the lattice temperature. This effective temperature falls towards, but does not reach, the lattice temperature during the exciton decay time of about 3 nsec. These statements are made for exciton densities* $\lesssim 10^{14}\,cm^{-3}$. As was concluded from the energy-dependent exciton decay times $\tau_{ex}(E)$ in Fig. 4, excitons are not in equilibrium with the lattice at 1.6 K. On the other hand, the analysis of Sec. III showed that the exciton distribution could be accurately fitted by the assumption of a time-dependent quasithermal equilibrium. The energy dependence of $\tau_{ex}(E)$ can therefore be explained by the following model: There exists a quasiequilibrium among the excitons with a temperature T higher than lattice temperature T_L, and T decreases noticeably during the exciton lifetime. In this model $I(E,t)$ is given by $I(E,t) \sim n_0(t)\, N(E)\, e^{-E/kT(t)}$. This formula assumes that a Maxwellian distribution of excitons can be established on a time scale short compared to the exciton decay time and also short compared to the variation of $T(t)$ in time. As a consequence, an exciton population in a cw experiment would also have a Maxwellian distribution with some average temperature above that of the lattice. The model therefore can also explain the previous successful theoretical description of the high-energy shape of exciton emission bands in cw experiments by a Boltzmann function.[11, 13, 24] It should be noticed that previous theoretical line-shape fits of cw emission bands[11, 13, 24] could be improved on the low-energy side for temperatures above ≈5 K, if the polariton density of states [Eq. (1)] would be used instead of the density of states of the uncoupled exciton. Below ≈5 K the above description becomes inadequate because the calculated exciton distribution would preferentially occupy states in the knee region, into which actual scattering rates are very low and insufficient for thermalization.

During the relaxation of excitons down the lower polariton branch we anticipate two kinds of scattering processes; those that give up energy to the lattice, thus shifting the distribution downwards in energy, and those that are randomizing processes in which the distribution loses no energy. In order for there to be a quasithermal distribution the latter must be at least as effective as the former. Except for the first 0.3 nsec after excitation, the randomizing processes cannot be provided by scattering of electrons and holes prior to exciton formation.[5] This formation process seems to be settled after a time of $\lesssim 0.3$ nsec, as can be concluded from the fast decay of the $A_{n=2}$ and $B_{n=1}$ exciton states (Table I).

As discussed Sec. III, scattering times for acoustic phonon emission are of the order of nanoseconds close to the knee of the dispersion curve. This fact is reflected by the slow time variation of exciton temperature $T(t)$ a few nsec after excitation (Fig. 5). However, the rapid change of $T(t)$ immediately after excitation, the fast exciton decay times $\tau(E)$ at kinetic energies $\gtrsim 1.5$ meV (see Fig. 4), and the independence of exciton line shape on excitation energy E_{exc} for $E_{exc} \gtrsim 2.556$ eV indicate very efficient phonon scattering at kinetic exciton energies $\gtrsim 2$ meV above E_T (Fig. 1).

An estimate for the time t_{ac} necessary to scatter an exciton of 3-meV kinetic energy (E_1) to an exciton state with 1.5-meV kinetic energy (E_2) can be derived from an equation for acoustic phonon scattering of electrons[25]:

$$t_{ac} = \frac{\rho\pi\hbar^4\sqrt{2}}{\Delta^2 (m^*)^{5/2}}\left(\frac{1}{E_2^{1/2}} - \frac{1}{E_1^{1/2}}\right). \tag{3}$$

Here ρ stands for the density of the crystal and Δ for the deformation potential of electrons. In the case of excitons at small wave vectors Δ can be replaced to first approximation by[15] $\Delta_{el} - \Delta_{hole}$ which is about 2 eV for CdS.[26] From Eq. (3) we get $t_{(3-1.5\,\mathrm{meV})\mathrm{ac}} \simeq 0.2$ nsec. Equation (3) cannot be used for kinetic exciton energies closer than about 1.5 meV to the knee since the formula is derived for parabolic bands and not for polaritons.

Thus, acoustic phonon *emission* is an important process to diminish the average kinetic energy of the exciton population. However, acoustic phonon *absorption* is insignificant for the low lattice temperature and the higher exciton temperature. Acoustic phonon scattering thus seems an unlikely mechanism for the establishment of a well-defined exciton temperature.

We are left with exciton-electron (hole) and exciton-exciton scattering. Exciton-electron (hole) scattering has to be considered only if one type of free carrier has a longer lifetime than the combined lifetime of free pairs and if excitation was above gap. Because we have no data on the electron lifetimes in our experiments we are only able to estimate the exciton-exciton scattering process. Assuming an interaction radius for excitons of four times the Bohr radius,[27] exciton densities of $10^{13}\,cm^{-3}$–$10^{14}\,cm^{-3}$ and mean kinetic energies corresponding to 10 K we estimate scattering times between 6 and 0.6 nsec. This scattering rate seems to be insufficient to establish a well-defined momentary equilibrium in our low-excitation density experiment, but a more detailed theoretical analysis of the randomizing processes has yet to be performed. The situation is different in experiments with high excitation densities, e.g., those of Leheny *et al.*[24] Their densities were 10^3 to 10^6 times higher than in our experiments, and in their case exciton-exciton scattering will be very efficient.

In the case of low densities, some details of the exciton relaxation process are still not clarified. A careful analysis and time resolution of the order 0.1 nsec will be required to distinguish between the emission from a downshifting ensemble of merely partially randomized excitons and a true thermal distribution.

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