Thermal relaxation of excitons in ZnSe and $Zn_{1-x}Mn_xSe$ diluted magnetic semiconductors

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We use time-resolved photoluminescence spectroscopy to measure the thermal relaxation of hot excitons in ZnSe-based diluted magnetic semiconductors at low temperatures ($T_{lat}<10$ K). Unlike other direct-gap semiconductors, the strong Fröhlich interaction in ZnSe semiconductors means that a spectral line associated with recombination of excitons accompanied by the emission of 1 or 2 optic phonons is easily visible in the photoluminescence spectra. The emission of the optic phonon relaxes the momentum selection rules so that any exciton in the band is allowed to recombine. Thus, the 1-LO and 2-LO phonon replica lines give a direct measure of the electronic temperature of the excitons within their bands. We find that the excitons relax within 300 ps to the lattice temperature, and that this relaxation can be accurately described by the emission of acoustic phonons through deformation-potential scattering theory. [S0163-1829(97)06108-0]

ZnSe-based heterostructures have recently become strong candidates for commercially viable blue solid-state lasers. The electronic states responsible for the laser emission in these materials are thought to be either excitonic or biexcitonic in nature.[1–3] Obtaining reliable data on the thermal relaxation of hot excitons in these materials would be particularly useful for design of high-efficiency electro-optics devices. Unfortunately, in most direct-gap semiconductors (such as ZnSe) momentum conservation considerations mean that only excitons near the Brioullin zone center can recombine and so no information about the thermal distribution of excitons can be obtained. However, in ZnSe the strong Fröhlich interaction between the electronic states and optic phonons means that recombination of excitons accompanied by emission of one or several phonons can be readily observed. Indeed, such phonon-assisted exciton luminescence has been used previously to determine energy relaxation rates in Cu_2O.[4] In this submission, we show how time-resolved photoluminescence from these phonon-assisted recombinations gives a direct measure of the instantaneous thermal distribution of excitons within their parabolic bands, allowing one to determine directly the thermal energy loss rate for hot excitons.

Samples used in these experiments consist of high-purity ZnSe and $Zn_xMn_{1-x}Se$ epilayers grown on GaAs substrates by molecular beam epitaxy. The epilayers are all 1 to 5 microns thick so that the strain caused by the lattice mismatch between the epilayers and the GaAs substrate has been completely relaxed by dislocations near the ZnSe/GaAs-substrate interface. Time-resolved and (CW) photoluminescence is obtained by photoexciting the epilayers with a frequency-tripled, mode-locked Nd-YAG laser. The resultant laser pulses at 354.7 nm were 80 ps wide and spaced 13.2 ns apart. The average power was kept less than 0.5 mW, and the laser spot nominally unfocused to a 1-mm spot to avoid heating. The samples were mounted onto a copper block inside a Janis variable-temperature cryostat, and the temperature was controlled by a computer.

Figure 1 displays a typical time-integrated photoluminescence (PL) spectrum from the 3-μm-thick high-purity ZnSe epilayer. These samples are of particularly high purity as can be seen by the detailed excitonic structure near 2.8 eV which shows a prominent free exciton line as well as several impurity-bound excitons at lower energy. Unfortunately, these zero-phonon recombination lines are not useful for measuring the thermal relaxation of excitons in their band, because momentum conservation requires that *only* those excitons with k vectors matching that of the out-going photon may recombine. This means that these emission lines really only sample the exciton population near $k=0$, at the bottom of the excitonic band.

A typical time-resolved spectrum from the same sample (shown in Fig. 2), concentrating on the zero-phonon bound- and free-exciton recombination lines, shows this difficulty clearly. The electrons and holes are excited well above the bottom of the band with significant amounts of excess energy. These electrons and holes cool to within a single optic

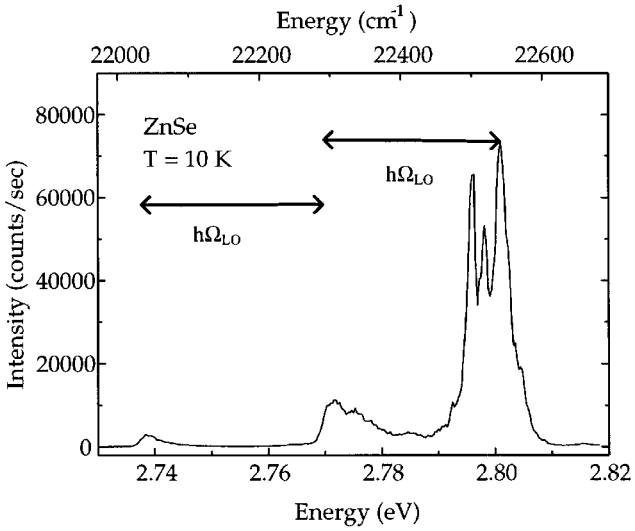

FIG. 1. Time-integrated photoluminescence spectrum of high-purity ZnSe at 10 K. Several free- and bound-exciton lines are seen at approximately 2.81 eV. At lower energy note the 1-LO and 2-LO phonon replicas of the free exciton.

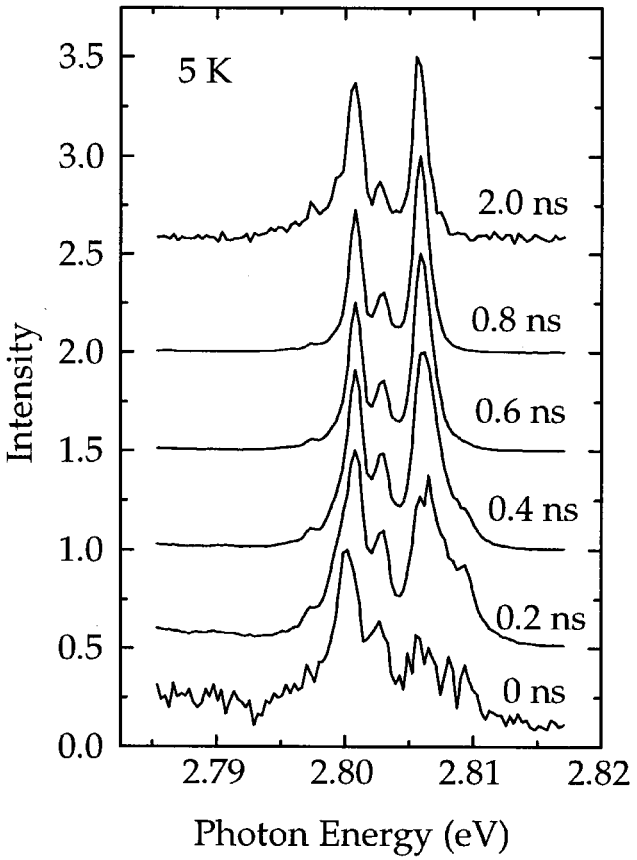

FIG. 2. Time-resolved spectra of the zero-phonon free- and bound-excitons PL lines near 2.81 eV.

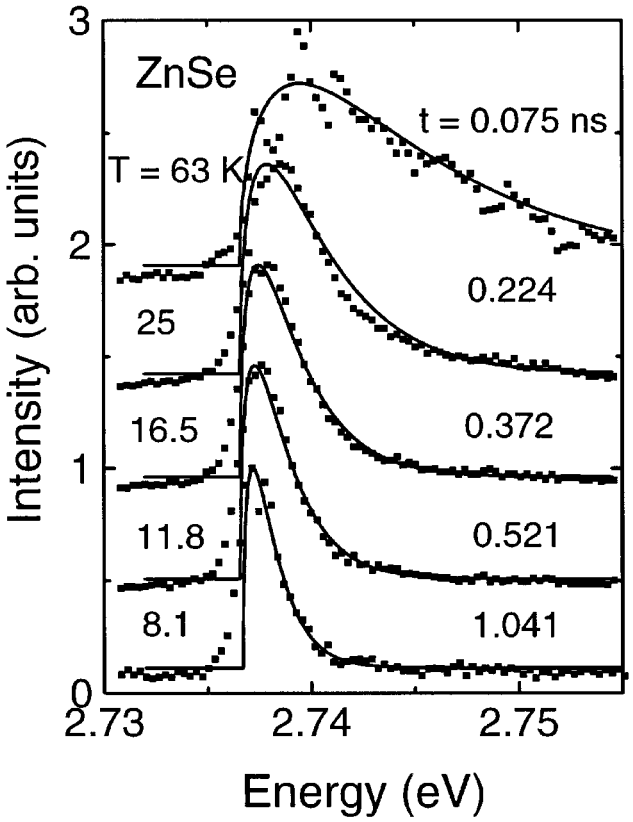

FIG. 3. Time-resolved spectra of the 2-LO phonon replicas of the free-exciton PL line. Solid lines are fits to the Maxwell-Boltzmann exciton line shape $\sqrt{E}e^{-E/kt}$.

phonon (30 meV or 300 K) of the band edge through the emission of optic phonons in a time less than 1 ps. However, once the excitons cool to this point they can only cool further through slower emission of acoustic phonons. Thus, one would expect that the excitons would have an initial temperature of at least 100 K, but should equilibrate to the lattice temperature (4.5 K) rapidly as the excitons emit acoustic phonons. The time-resolved spectra of the zero-phonon exciton luminescence shows little evidence for this expected cooling. While some small changes are seen at the earliest times between the intensities of the free exciton and the two bound exciton lines, virtually no change is seen in the relative intensities of these lines throughout their lifetimes. This is merely a reflection of the momentum selection rules described above: the zero-phonon exciton PL lines only sample the very bottom of the exciton band and so are completely insensitive to the thermal distribution of excitons within the parabolic bands.

If one looks closely at the PL spectrum in Fig. 1, one can also see several relatively broad, asymmetric PL lines at lower energy, each separated by a multiple of 30 meV from the zero-phonon exciton PL lines. These lines are the result of excitons recombining and emitting *both* a photon and one or two longitudinal-optic phonons. The restrictive momentum selection rules are removed because the phonon takes up the additional momentum of the exciton. Thus, for these phonon replicas of the exciton PL line, *any* exciton in the band may recombine and emit a photon which is characteristic of the kinetic energy of the exciton as it recombines. In fact, the *intensity* of the emitted PL at that energy is proportional to the population of excitons at that kinetic energy. The expected lineshape for these phonon replicas is therefore just the density of states multiplied by a Boltzmann factor: $\sqrt{\varepsilon}e^{-\varepsilon/k_BT}$, where $\sqrt{\varepsilon}$ is the three-dimensional density of states for the exciton, and T is the exciton temperature.

In these experiments, we look at the 2-LO phonon replica rather than the 1-LO replica because the latter luminescence line has superimposed on it several sharp peaks associated with the two-electron Auger PL lines (see Fig. 1). In contrast (see Fig. 3), the 2-LO PL line is quite clean and displays exactly the expected form for the PL intensity versus energy. Note the broad asymmetric PL lines with long exponential tails on the high-energy side. Just after the laser pulse the line is quite broad (indicating the higher temperature) but narrows quickly. The solid lines are fits at each time to the 2-LO PL line. The temperatures are shown for each spectrum. Note that just after the laser pulse, the exciton temperature is seen to be 90 K—well above the lattice temperature of 4.5 K. However, the exciton temperatures cool rapidly to the lattice temperature within several hundred picoseconds. The exciton temperature determined from these fits as a function of time is shown as squares in Fig. 4. Note also that the low energy edge of the 2-LO PL line is quite sharp and does not shift with time after the laser pulse, despite the fact that the excitons display initial temperatures approaching 100 K. This indicates that the *lattice temperature* is not changed locally by the absorption of the laser pulse. (Note that if the lattice temperature were locally raised by absorption of the

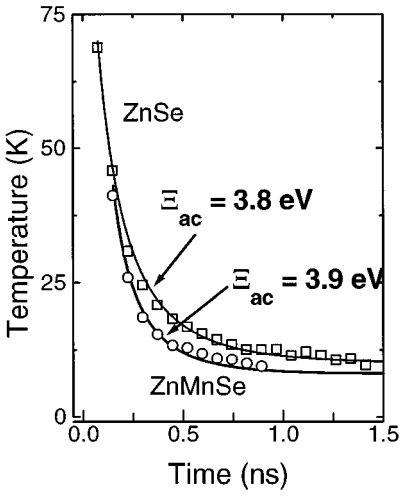

FIG. 4. Temperatures extracted from fits to data as in Fig. 3, shown as a function of time after excitation by the laser pulse. Squares are data obtained from the high-purity ZnSe sample, circles are data obtained from the 2% $Zn_xMn_{1-x}Se$ epilayer. Solid lines are fits to Eq. (1) as described in the text.

laser pulse, one would expect to see an initial *redshift* of the photoluminescence line.)

Similar measurements have been made in $Zn_{1-x}Mn_xSe$ for Mn concentrations of 2 (circles, Fig. 4) and 4%. The thermal relaxation of excitons in these magnetic semiconductors is nearly identical to that seen in the pure ZnSe epilayer. This is to be expected since acoustic phonon emission is thought to be the dominant energy relaxation process for excitons in these materials. While the elastic coefficients of the epilayer change slightly with the addition of Mn into ZnSe, the physics underlying the phonon emission rate would not be expected to change dramatically.

We model this phonon emission by using standard deformation potential scattering theory. For acoustic phonons, the average energy loss rate may be expressed as[4]

$$\Gamma_{\rm ac}=\left\langle \frac{dE}{dt}\right\rangle = \frac{8\sqrt{2}}{\pi^{3/2}}\frac{\Xi_{\rm ac}^2 m^{5/2}}{h^4\rho}(k_B T_e)^{3/2}\left(1-\frac{T_l}{T_e}\right) \qquad (1)$$

where $\Xi_{\rm ac}$ is the acoustic deformation potential, m is the exciton mass, ρ is the mass density of ZnSe, T_l is the lattice temperature, k_B is the Boltzmann constant, and T_e is the average electronic temperature. Given the energy loss rate $\Gamma_{\rm ac}$, the change in temperature dT_e per time interval dt is given by $dT_e=\Gamma_{\rm ac}(T_e)dt/k_B$. Using the initial exciton temperature measured in our experiments and the known effective masses and densities of ZnSe,[5] we can numerically integrate this expression to determine the exciton temperature as a function of time. The only free parameter is thus deformation potential, $\Xi_{\rm ac}$. The solid lines in Fig. 4 are best fits to the thermal relaxation data. We find that the optimal fit to the data yields $\Xi_{\rm ac}=3.8$ eV for pure ZnSe and $\Xi_{\rm ac}=3.9$ eV for the 2% $Zn_xMn_{1-x}Se$ epilayer.

To summarize, we have shown that it is possible to measure the instantaneous thermal distributions of excitons in ZnSe and related compounds by time-resolved photoluminescence of the 2-LO replica of the free-exciton line. We find that the initial relaxation of excitons to within 100 K occurs very rapidly, probably within several picoseconds. Final thermalization with the lattice occurs relatively slowly through the emission of acoustic phonons. We model this relaxation mode using standard deformation potential scattering theory and determine the acoustic deformation potential $\Xi_{\rm ac}$ equal to 3.6 eV.

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