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Hot-exciton luminescence and energy transfer into *d*-electron states in $Zn_{1-x}Mn_xSe$

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Rapid electronic energy transfer from photoexcited electron-hole pairs into *d*-electron states of the Mn^{2+}ion in the diluted magnetic semiconductor $Zn_{1-x}Mn_xSe$ can serve as an efficient channel to reduce the role of thermalized excitons in the recombination spectrum. This circumstance allows clear observation and characterization of luminescence from nonthermal, or "hot," excitons, which have rapidly relaxed via multiple longitudinal-optical (LO) phonon emission to the excitonic band-gap state (E_{gx}). A resonant enhancement in the hot-exciton emission is observed whenever the photon energy of excitation is exactly an integer number of LO phonons above E_{gx}. Tuning of the gap states in a magnetic field serves as a means of sweeping through the resonant condition for the identification of the hot luminescence. Strikingly, the amplitude variations in the hot-exciton luminescence are reflected in the Mn-ion internal *d*-electron emission at yellow wavelengths.

I. INTRODUCTION

The phenomenon of luminescence from nonthermal excitons has been extensively studied in II-VI semiconducting compounds,[1] revised recently in the context of distinguishing such hot luminescence (HL) from resonant Raman (RR) processes.[2,3] Both processes involve spectral features which are sharp in energy, separated by increments in the LO-phonon energy ($\hbar\omega_{LO}$) from the photon energy of (laser) excitation, and strongly enhanced at emission energies corresponding to intrinsic or extrinsic excitonic band-gap resonances. Photoluminescence excitation (PLE) spectroscopy has been extensively used in the study of the hot-exciton process,[4-6] which phenomenologically differs from the RR process in possessing an "energy memory" of the monochromatic excitation but not a phase memory. In order to observe HL emission clearly, however, it is generally necessary to provide some mechanism for quenching the normally dominant luminescence arising from thermalized excitons. In earlier studies, efficient nonradiative transitions (by defects and impurities) performed this function in bulk materials. In one recent instance, quantum wells with thin barrier layers were designated to reduce the formation of thermalized excitons by rapid electron-hole pair escape via tunneling from the active layers.[2]

The Mn-based diluted magnetic semiconductors (DMS) exhibit a rich set of physical phenomena,[7] to which we add in this paper aspects of the exciton HL process. In this work we take advantage of two specific features of the wide band-gap $Zn_{1-x}Mn_xSe$: (i) the Mn^{2+}-ion *d*-electron excitations (including the emission derived from these) and (ii) the giant Zeeman effect at the band-edge states. The band-gap energy of $Zn_{1-x}Mn_xSe$ at low levels of Mn concentration ($x<0.05$) is approximately 2.80 eV at low temperatures. Hence several of the five internal 3*d* shell optical transitions with respect to the ground state of the ion (of which the lowest yields the well-studied yellow luminescence at approximately 2.1 eV) occur below this energy. Though such *d*-*d* transitions are spin forbidden (electric dipole) in first order, the crystal field breaks the symmetry sufficiently such that the yellow emission can be a dominant feature in the overall photoluminescence (PL) from the crystal, for Mn concentrations on the order of 1 at. %. (We note that as a practical application, the *d*-electron emission is used in electroluminescent display devices.) At the concentration and temperature studied here ($x=0.05$ and mainly at $T=2$ K), both the 2.1-eV band and the excitonic band-gap emission are easily measurable in photoluminescence—a condition which facilitates examination of the relationship between the two. The problem is also of applied interest since the recent development of *pn*-junction light emitters based on ZnSe suggests that, e.g., LED devices might be developed at short visible wavelengths in these materials, including a semiconductor such as $Zn_{1-x}Mn_xSe$.

As is well known, the giant Zeeman effect occurs due to an exchange interaction between the *s* and *p* band-edge states and the Mn 3*d* shell electrons. Application of a magnetic field effectively "tunes" the band gap (by spin splitting the *s* and *p* states), in our case over an energy range of ≈ 50 meV below the zero-field gap energy. This technique is utilized as an alternative method to sweeping the excitation energy for PLE spectroscopy.

II. EXPERIMENTAL RESULTS

The samples used in this work were epitaxial layers of $Zn_{1-x}Mn_xSe$, grown by molecular beam epitaxy on GaAs substrates. A range of concentrations was examined; however, we focus here on a 1.5-μm-thick sample with $x=0.05$. Due to the anomalous "bowing" of the band gap in $Zn_{1-x}Mn_xSe$ at low Mn fractions,[8] the excitonic band-gap energy (E_{gx}) for this sample is very nearly the same as for bulk ZnSe at low temperatures. The samples were mounted onto a coldfinger and immersed in superfluid helium in a superconducting magnet with direct optical access. Some spectra were also taken at higher temperatures as reported below. Optical excitation was achieved with a stilbene 420 laser, pumped by a continuous-wave Ar^+-ion ultraviolet laser. The dye laser provided a tuning range of photon energies from about 2.63 to 2.95 eV. The samples were irradiated at a moderate excitation level of 1–10 $\mathrm{W/cm^2}$. One indication of the quality of the material is shown in the inset of Fig. 3 below which displays the reflectance spectrum near the excitonic band gap, with a strong reflectance anomaly in the range of 2.802–2.804 eV.

Figure 1 shows the PL spectra obtained at $T=2$ K for the $\mathrm{Zn_{0.95}Mn_{0.05}Se}$ epitaxial film in the vicinity of the band gap, as a function of the photon energy of the excitation. More specifically, the energy range for the emission is displayed near the excitonic band gap, E_{gx}, while the excitation energy ranges from approximately one LO-phonon energy $\hbar\omega_{\mathrm{LO}}$ to nearly four-LO-phonon energies above E_{gx}. The PL spectrum is punctuated by sharp features which originate from hot-exciton emission, resonantly enhanced at E_{gx}. The enhancement occurs whenever the photon energy of excitation creates an electron-hole pair with an excess energy an integer multiple $nh\omega_{\mathrm{LO}}$ with respect to E_{gx} (where $h\omega_{\mathrm{LO}}=31.5$ meV in ZnSe). LO-phonon processes up to $n=4$ can be seen in the figure. At the excitonic band gap E_{gx} there are two features present; these we assign to free (FX) and localized excitons (LX), respectively.[9] In Fig. 1, the FX and LX components can be most easily viewed at the highest energy of excitation (at about 2.93 eV), and correspond to PL emission at 2.798 and 2.792 eV, respectively. The issues of localization in alloy potential fluctuations in a DMS crystal have been detailed, e.g., in Ref. 9, and will not be discussed further here. At this energy of excitation, the FX and LX emissions are chiefly due to the thermalized exciton luminescence. Such a finite thermalized PL "background" notwithstanding, the efficient draining of photoexcited electron-hole pair energy into the Mn^{2+}-ion d-electron states, as discussed below, significantly facilitates the observation of the nonthermal HL emission under the resonantly enhanced conditions. In particular, the resonance enhancement is clearly seen to occur at the FX energy (to which the assignment E_{gx} is applied henceforth). Although not focusing on the temperature dependence of the HL effect in this paper, we mention that the sharp emission features remain clearly visible at least to $T=100$ K, in part due to the reduction in the thermalized PL component with increasing temperature.

The effect of magnetic-field tuning on the emission processes is illustrated in Fig. 2, wherein the range of fields up to $B=6$ T, the lowest spin-split exciton state ($m_j=-\frac{1}{2}$ to $m_j=+\frac{3}{2}$ conduction-to-valence band transition) is redshifted in excess of one LO-phonon energy. As also predicted for $x=0.05$, the d-electron magnetization reaches saturation in the high end of our field range; this is very clearly seen in the "saturation" of the Zeeman shifts of emissions near E_{gx}. The inset of the figure shows the first-order HL process in more detail (emission at $\hbar\omega_{\mathrm{exc}}-n\hbar\omega_{\mathrm{LO}}$, with $n=1$), where the HL phenomenon is brought into a sharp resonance over a small field range at $B\approx0.4$ T. At somewhat higher fields, Fig. 2 shows clearly how the two LO-phonon resonance enhancement ($n=2$) in the HL emission is reached at a field of approximately $B\approx2.2$ T. The HL emission was checked to be circularly polarized as expected from the angular momentum selection rules (the excitation was linearly polarized). Note that quite apart from the HL effect, the average exciton emission intensity increases in the B field due to diamagnetic effects; this explains the gradual further increase in the peak amplitudes, especially for the free exciton component (most pronounced for $B>4$ T). Finally, consistent with observations of Fig. 1, we see again that the HL enhancement occurs distinctly at E_{gx} corresponding to free, and not localized, excitons.

To obtain direct evidence of the role of the Mn^{2+}-ion d-electron states in the reduction of the thermalized PL (the latter being a relatively slow process which involves acoustic phonon-assisted relaxation at the low lattice temperatures in question), we also studied the relationship between the near band-edge excitonic emission (described above) and the yellow luminescence from the Mn^{2+}-ion lowest d-electron transition. Figure 3 shows the PLE spectrum of the yellow emission (monitored at $\hbar\omega_{\mathrm{Mn}}=2.1$ eV), together with the excitonic PLE spec-

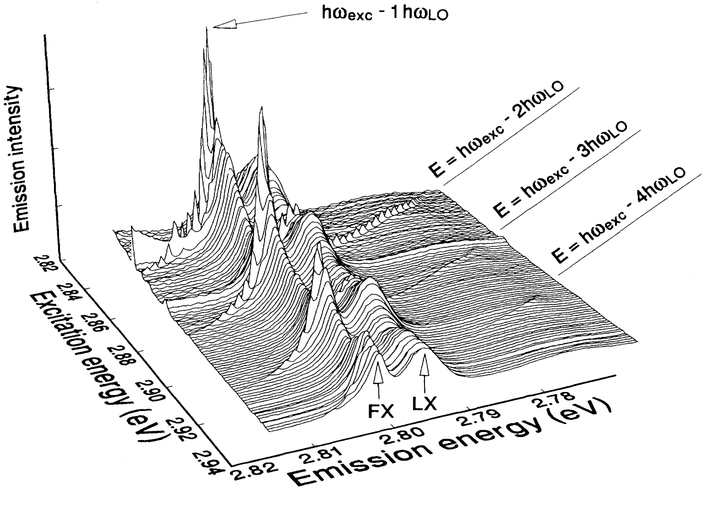

FIG. 1. Emission spectrum from a $\mathrm{Zn_{0.95}Mn_{0.05}Se}$ epitaxial layer as a function of photon energy of excitation at $T=2$ K. The hot-exciton emission at resonance is indicated by the long arrow for the first-order process ($\hbar\omega_{\mathrm{exc}}-1\hbar\omega_{\mathrm{LO}}$). The evolution of the higher-order emissions are indicated by the appropriate lines. The free (FX) and localized (LX) exciton thermalized PL contributions are also indicated.

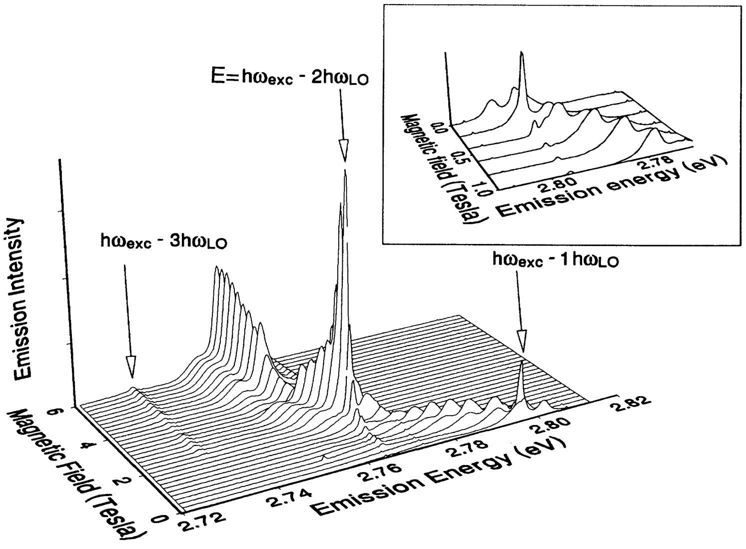

FIG. 2. Tuning of the HL resonance condition at the excitonic band gap by a magnetic field from $B=0$ to 6 T. The inset shows the emission spectrum in more detail from $B=0$ to 1 T.

trum (spectrally integrated over a 20 meV range at E_{gx}), over an energy range of several LO phonons in the excitation energy. The line shape of the yellow emission remained unchanged and independent of the excitation energy. To accurately demark the exciton resonance (beyond the PL observation of the FX and LX features), the inset shows the reflectance spectrum near E_{gx} (energy scale expanded). Note that at and above the one LO-phonon exciton HL resonance, the PLE spectra for the yellow and the blue emissions exhibit complementary behavior: at a HL maximum, the *d*-electron emission shows a minimum, and vice versa. This demonstrates unambiguously the competing nature of the processes, i.e., the modulation in the conversion of electron-hole pair energy into the *d*-electron excitations. Finally as the photon energy of excitation approaches E_{gx} below the one LO-phonon resonance, the yellow emission first undergoes a distinct maximum (at $\hbar\omega \approx 2.813$ eV in Fig. 3) before exhibiting a small anomaly (arrow at $\hbar\omega = E_{gx}$) which is spectrally well correlated with both the excitonic reflection and the FX peak in luminescence.

As another characteristic of the process of electron-hole pair energy conversion to the *d*-electron excitation, Fig. 4 shows the PLE spectrum of the yellow emission (at $\hbar\omega_{\mathrm{Mn}} = 2.1$ eV) as a function of temperature from $T=15$ to 90 K. The most obvious temperature-dependent effect is the reduction of the strong maximum between E_{gx} and the one LO-phonon resonance. At the same time, a finite enhancement effect near E_{gx} itself is seen to be present throughout the temperature range.

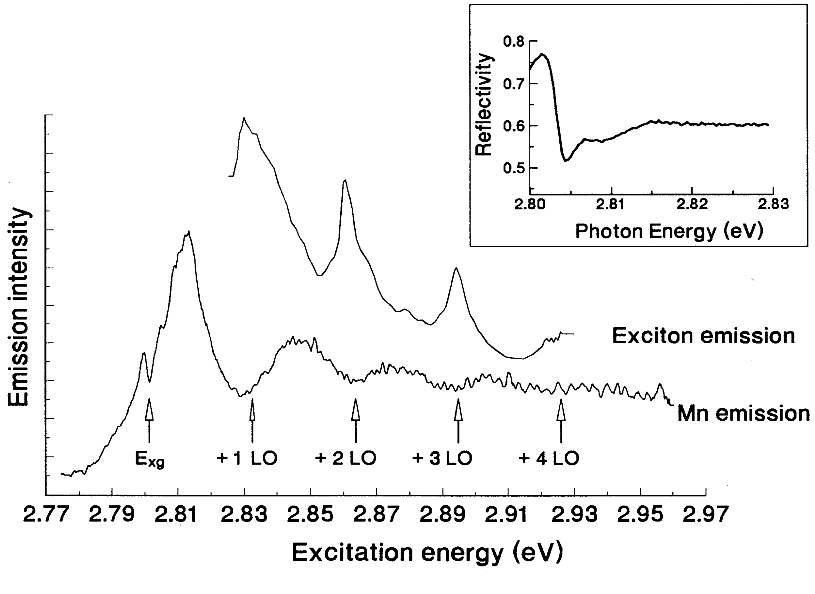

FIG. 3. Emission intensity for the "blue" exciton emission and the "yellow" Mn^{2+}-ion *d*-electron emission as a function of the photon energy of excitation. The excitonic band gap (E_{gx}) and the positions of first four orders of the LO-phonon "ladder" are indicated. The inset shows the reflectance spectrum near the excitonic resonance. The amplitudes of the two traces are not on the same scale.

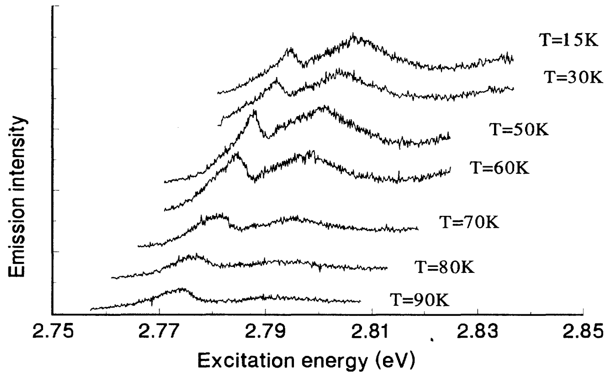

FIG. 4. The excitation spectrum of the *d*-electron emission as a function of temperature from $T=15$ to 90 K. The spectra have been displaced vertically for clarity.

III. DISCUSSION

The experimental evidence presented above indicates that under resonant conditions at the excitonic band gap, the excitonic HL emissions are selectively enhanced over the spectrally broader thermal components, thus reflecting the energy memory in the process. More precisely, the experiment shows that the photon energies of the resonance enhancement occur with the multiple LO-phonon ladder coinciding with the free, not localized, exciton states.

It has long been recognized that in the wide band-gap DMS materials, normal interband transitions coexist, and interact, with the transitions due to the half-filled Mn^{2+}-ion *d*-electron shell.[10,11] However, to our knowledge there are no experimental or theoretical observations of the HL effect in this context. Here we try to draw the observations summarized in Figs. 1–4 together in a phenomenological discussion.

Following the initial photogeneration of an electron-hole pair in a semiconductor such as $Zn_{1-x}Mn_xSe$, the subsequent energy relaxation-recombination process is generally thought to proceed via two main pathways: (i) the electron-hole pair energy relaxation to the band-edge states, followed by thermalization and exciton formation steps and eventual recombination (with a radiative lifetime typically in excess of 100 psec); or (ii) the conversion of the electron-hole pair energy prior to the recombination step directly into the *d*-electron excitation (presumably in some form of inelastic collision, such as akin to an Auger process[12]), followed by radiative relaxation of the *d*-electron back to its ground state. However, as shown in our experiments, electronic energy can escape radiatively also quite efficiently in the form of hot excitons, i.e., electron-hole pairs that are created initially at an excess energy ΔE relative to the excitonic band gap, which is precisely an integer number of LO phonons ($\Delta E = n\hbar\omega_{LO}$). The strength of the Frohlich interaction in a polar semiconductor such as $Zn_{1-x}Mn_xSe$, together with the large radiative matrix element for the exciton states, then leads to the observation of the resonance enhancement effects such as in Figs. 1 and 2. From this phenomenological viewpoint, some of the electron-hole pairs remain Coulomb correlated *throughout* the relaxation-recombination process. A question arises immediately, however, about the initial state at which they are created due to the small momentum of the absorbed photon. We take the view here that phonon-assisted (i.e., indirect) absorption is required for the existence of such an all-exciton chain of events, as suggested earlier by Permogorov and co-workers.[1]

In terms of the actual rates for the various relaxation and recombination processes, there are very few direct quantative results in the literature. Hefetz *et al.* showed that the electron-hole pair capture by the Mn ion could not be longer than a few psec in $Zn_{0.85}Mn_{0.15}Se$.[13] On the other hand, Pelekanos *et al.* attempted to measure the hot-exciton decay time in a ZnTe quantum well and showed that this too occured on a psec time scale (or less).[2] In addition, the typical one LO-phonon–hot-electron relaxation time in ZnSe can be theoretically estimated to be on the order of 100 fsec per phonon (and less), based on the calculated strength of the Frohlich interaction. All of these times are considerably shorter than either the electron-hole pair thermalization time at the band extrema by acoustic phonons (on the order of 1 nsec), the exciton formation time from such "warm" electron-hole pairs (estimated to be about 100 psec in time-resolved experiments)[14] as well as the radiative recombination time of thermal excitons (also measured to be about 100 psec or longer). Semiquantitatively, and in a rate equation spirit, we can then understand the heirarchy of effects which determine the observations depicted in Figs. 1–3, namely, that the hot-exciton luminescence and the Mn^{2+}-ion *d*-electron emission can be seen to complete with each other, so that the normally efficient energy transfer into the *d*-electrons states can be shunted by the HL process if the initial state is correctly prepared ($\Delta E = n\hbar\omega_{LO}$). In fact, from the depth of modulation of the PLE data in Fig. 3, we can estimate that the fraction of photons which are absorbed in the indirect (phonon-assisted) process to the hot-exciton states must exceed 10% of the total.

For photon energies of excitation below $\hbar\omega_{exc} < E_{gx} + \hbar\omega_{LO}$, the data in Figs. 3 and 4 show an interesting indication of the importance of the effective exciton temperature in the energy conversion to the *d*-electron states under circumstances where the hot-exciton effects are not dominant. Recall that the exciton reflectance anomaly is also present in the PLE spectrum of the yellow emission (at E_{gx}) showing unambiguously that excitons can indeed be responsible for the *d*-electron luminescence. On the other hand, the presence of an absolute maximum at about $\hbar\omega_{exc} = 2.813$ eV strongly suggests that "warm" excitons (either in the 1*S* or excited states) are considerably more effective than cold excitons (for reference, we note that the exciton binding energy in bulk ZnSe is about 17 meV). The temperature dependence in Fig. 4 also supports the notion of a warm-exciton contribution to the *d*-electron excitation process by the following argument. With increasing temperature, the warm-exciton PLE peak is seen to decrease in Fig. 4, presumably due to the increasing thermal dissociation of the excitons to the free *e-h* pair states. This is expected due to the large exciton–LO phonon coupling which is known to lead to such rapid lifetimes, e.g., in smearing out the observation of the exciton state in absorption in bulk ZnSe for temperatures beyond $T=100$ K. The peak at the exciton ground state in Fig. 4 is a measure of the absorption process, followed in the temperature range in question by the thermal generation of warm excitons. This provides the argument for the presence of the distinct (broadened) PLE maximum at the exciton absorption maximum at $T=90$ K in the figure.

In conclusion, we have shown how hot-exciton luminescence and the excitation of the Mn^{2+}-ion *d*-electron states are competing processes in a DMS material such as $Zn_{1-x}Mn_xSe$. The HL phenomenon shows a distinct resonance condition at the free exciton band gap. When such enhancement occurs, the yellow *d*-electron luminescence is substantially reduced, and vice versa. Although our work has focused on cryogenic temperatures, it may be possible to take advantage of the enhanced excitonic processes in quantum-well structures to promote the exciton–to–*d*-electron energy conversion in *pn*-junction electroluminescent devices.

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