Photoluminescence in semimagnetic $Zn_{1-x}Mn_xTe$

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Luminescence in photoexcited $Zn_{1-x}Mn_xTe$ has been studied for three dilute alloy compositions ($x=0.001$, 0.011, and 0.016) under a wide range of excitation and in zero external magnetic field. We find that the bound-exciton localization energy is composition dependent, evidently due to an exchange-induced contribution by the paramagnetic Mn ions. Under high-intensity excitation we have observed electron-hole plasma (EHP) emission from all the samples studied. For the line-shape analysis of the EHP emission, a simple model is introduced that takes alloy-compositional fluctuations into account. The EHP emission for the $x=0.001$ material yields plasma parameters which are consistent with the formation of an electron-hole liquid, while in samples with higher Mn concentration there is no evidence for such formation.

I. INTRODUCTION

In a semimagnetic semiconductor of the type $A^{II}_{1-x}Mn_xB^{VI}$ the spin-spin exchange interaction between bandlike electrons and the localized magnetic moments of the magnetic ions leads to interesting behavior, such as giant g values and the bound—magnetic-polaron effect.[1] The latter is an example of exchange-induced effects which appear even in the absence of an external magnetic field and have been observed to contribute to anomalous light scattering and luminescence spectra associated with near—band-gap excitations.[2]

The main focus of recent spectroscopic work in several II-VI semimagnetic alloys has involved excitonic and impurity related phenomena.[3] At the same time there is a notable lack of experimental work concerning the influence of the Mn-ion exchange interaction on a photoexcited electron-hole plasma (EHP). This could be of importance, for example, in contributing to the stability of the EHP or the formation of an electron-hole liquid (EHL) in a semimagnetic semiconductor. Elsewhere Pashitskii and Ryabchenko have speculated that an exchange-induced magnetic ordering could occur in an EHP in such a material.[4] Furthermore, the role of finite-alloy disorder effects in influencing the luminescence spectra has not been clearly assessed.

This investigation was undertaken to study the role of the Mn ion in photoexcited $Zn_{1-x}Mn_xTe$ in the absence of externally applied magnetic fields. Since little published work is generally available on the interband recombination spectra in this alloy, we report here results which include the spectroscopy of both excitons and the EHP. We have examined the photoluminescence of ZnMnTe under a wide range of photoexcitation for three alloy compositions ($x=0.001$, 0.011, and 0.016) where the Mn-ion spin system remains paramagnetic. At low excitation the observed spectra reveal free-exciton emission which has been used to assign values for the energy gap for this composition range. Photoluminescence associated with an acceptor bound exciton shows an enhancement in its binding energy with increasing Mn content, an effect that we attribute to the exchange interaction between the exciton and the $3d$ electrons of the Mn ion. We have also studied the EHP emission as a function of excitation intensity and composition. The data for the $x=0.001$ material indicates that the plasma density saturates both as a function of effective plasma temperature and a function of excitation intensity. This strongly suggests EHL formation for this composition. In order to derive EHP parameters from the emission spectra of samples with a higher concentration of Mn, we have applied a simple model for a line-shape calculation which accounts for the alloy compositional fluctuations in our mixed crystals.

II. EXPERIMENTAL RESULTS AND ANALYSIS

The samples used in this study were nominally undoped single-crystals of $Zn_{1-x}Mn_xTe$ grown by Professor J. Furdyna at Purdue University. The composition was determined by microprobe analysis to an accuracy of 0.1%. No particular effort was made in our experiments to orient the samples which were obtained by cleaving bulk pieces.

Photoluminescence data were obtained by excitation with a N_2 laser ($\hbar\omega_{ex}\simeq 3.65$ eV, pulse width 10 nsec). The peak incident intensity at the samples varied between 10^3–10^6 W/cm^2. Luminescence emission was collected perpendicular to the excited surface and focused on the entrance slit of a monochromator equipped with a S-11—type photomultiplier. The photodetector output was analyzed by a microcomputer. The on-line computer was also employed to drive the monochromator and trigger the laser.[5] The samples were immersed in liquid helium ($T=2$ K), but considerably higher electronic temperatures could be generated, as discussed below.

A. Low-excitation regime

Under low-excitation intensity the photoluminescence (PL) of ZnMnTe ($x=0.001$) resembles the spectra of pure ZnTe (Fig. 1). It is dominated by a single strong emission peak at 2.377 eV (labeled A), surrounded by a few weaker lines which include a relatively sharp LO-photon replica.

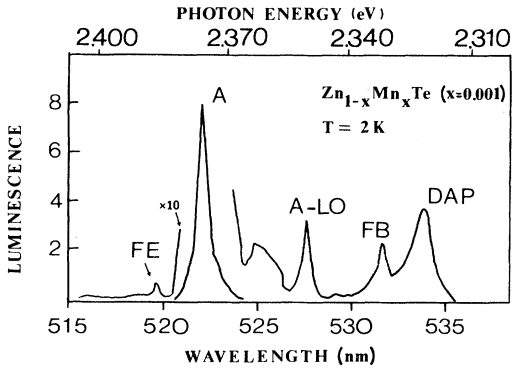

FIG. 1. Photoluminescence spectrum of $Zn_{1-x}Mn_xTe$ ($x=0.001$) under low-intensity excitation.

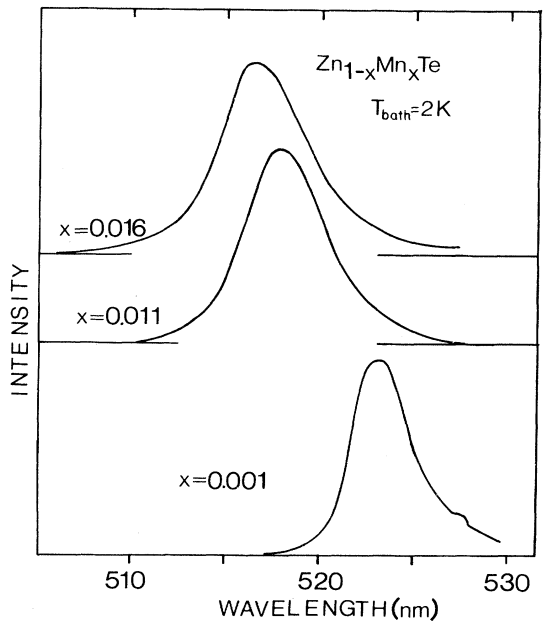

FIG. 2. Photoluminescence spectra under high-intensity ($I_0=1$ MW/cm^2) excitation.

The free-exciton emission (FE) is clearly identifiable at 2.385 eV as is the emission from a donor-acceptor pair (DAP) together with free-to-bound (FB) luminescence (Dean[6] and references therein). By analogy with the well-studied emission spectra of ZnTe, we associate the principal line with a neutral-acceptor bound exciton having a localization energy of ~ 8 meV. Since this is only slightly larger than the corresponding value for ZnTe (6 meV), the effect of exchange interaction between the localized Mn-ion magnetic moment and the three-particle carrier complex contributes at most a small correction for this composition. The main direct effect by the Mn is a "rigid" shift of the band gap. Taking the free-exciton binding energy to be 13 meV (as for ZnTe), we obtain 2.398 eV for the energy gap of the $x=0.001$ material at $T=2$ K. Here and below, we assume that the (possible) effective-mass changes remain small in the alloy range of interest.

Much of the fine structure seen in Fig. 1 disappears in the luminescence spectra of the $x=0.011$ and 0.016 samples, lost most likely due to broadening caused by alloy potential fluctuations. A single strong-emission line dominates the spectra for both compositions. This can still be readily associated with the now broadened acceptor bound exciton. A small free exciton peak can also be observed on the high-energy side of this emission. By employing the (reasonable) approximation of a constant free exciton binding energy, the values of the energy gaps for the three alloy compositions, all at $T=2$ K, can be summarized readily as follows: $x=0.001$, $E_g=2.398$ eV; $x=0.011$, $E_g=2.422$ eV; $x=0.016$, $E_g=2.436$ eV. The localization energy of the bound exciton is now found to increase from 8 meV for $x=0.001$ to 13 and 19 meV for the $x=0.011$ and 0.016 material, respectively. Such an increase is likely to have a significant component from the exchange interaction between the exciton's charge carriers (the outer electron) and the Mn-ion spins within its Bohr orbit, as has been demonstrated recently in experiments involving the donor bound exciton in $Cd_{1-x}Mn_xSe$.[7] For the simpler configuration of a neutral donor or acceptor the exchange contribution has been shown to have two contributions to the (inhomogeneous) spin splitting at a low temperature.[8] One contribution is due to a trend toward local spin alignment within the Bohr orbit (the bound—magnetic-polaron effect) and the second results from a net magnetization presented by a finite number of Mn-ion spins within this volume. [We note here that in the absence of accurate values for the conduction and valence band exchange coefficients in ZnMnTe, more quantitative estimates about the spin-splitting of the initial (bound exciton) and the final (acceptor) state involved in the optical transition remain presently uncertain.]

B. High-excitation regime

As the excitation intensity increases to approximately 2×10^4 W/cm^2, the bound-exciton line begins to broaden for all compositions studied. Above 10^5 W/cm^2 the luminescence is completely dominated by a single broad-emission band which is identified by us as a contribution from an EHP and shown in Fig. 2. Broad emission bands observed earlier in similarly excited pure ZnTe (but mainly at lattice temperatures higher than those encountered here) have been interpreted by considering free exciton-exciton (x-x) and free exciton-hole (x-h) inelastic scattering.[9] Theoretical calculations have also shown how such spectra can be identified by their characteristic emission energy and line shape.[10] In our case the energetic position of the emission peaks in Fig. 2 and their shift with excitation intensity are not compatible with those anticipated for inelastic exciton spectra. Additionally, estimates of free-exciton screening (Mott criteria) for the excitation densities and temperatures encountered in our experiments further discount the likelihood of the x-x and x-h contribution. In contrast the observed behavior of the luminescence agrees well with that for an EHP. Band-gap renor-

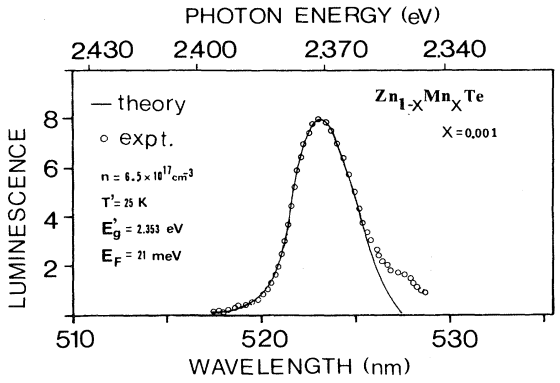

FIG. 3. EHP luminescence of $Zn_{1-x}Mn_xTe$ ($x=0.001$) vs photon energy. Solid line represents the best fit to the spectrum. The fitting parameters are also shown on the figure.

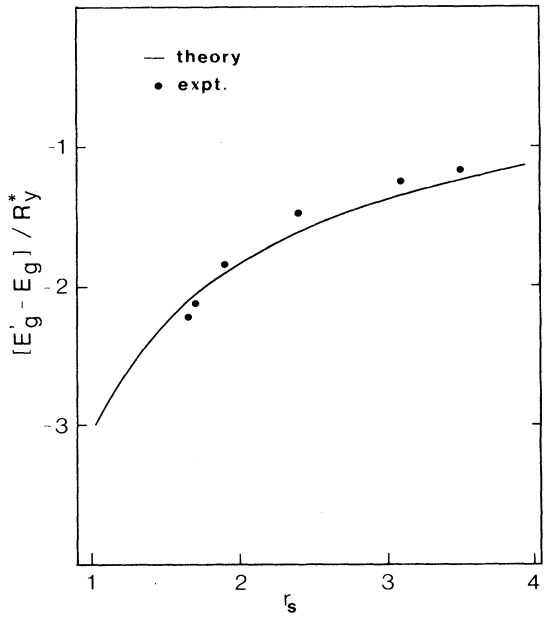

FIG. 4. Experimental and theoretical renormalized band-gap energy vs reduced pair separation for $Zn_{1-x}Mn_xTe$ ($x=0.001$). Experimental points were obtained from the best fit to the EHP luminescence, while the theoretical curve is from Ref. 12. Energy is in units of effective Rydberg.

malization effects lower the emission energy of the EHP so that significant spectral overlap with the bound-exciton energy region occurs. This leads to some ambiguity about the gradual disappearance of the bound-exciton contribution, namely, whether these excitons are screened by the plasma in a Mott-type transition or whether exciton luminescence becomes simply undetectable due to (acceptor) population saturation effects. (A small but evident LO-phonon replica of the bound exciton was still detectable in the $x=0.001$ sample suggesting that not all of the bound excitons need be screened at our maximum excitation intensity.)

In order to study the carrier density and the effective plasma temperature as a function of excitation intensity, we have fitted the measured EHP luminescence to the following expression which describes radiative recombination from an EHP in the absence of momentum conservation[11]:

$$I(\hbar\omega)=I_0\int_0^{\hbar\omega'} E^{1/2}(\hbar\omega'-E)^{1/2} \times\{1+\exp[(E-E_f^h)/kT]\}^{-1} \times\{1+\exp[(\hbar\omega'-E-E_f^e)/kT]\}^{-1}dE \ . \quad (1)$$

Here $E_F^{e,h}$ is the quasi-Fermi energy determined from

$$n=a\int_0^{\infty} x^{1/2}[\exp(x-E_F/kT)+1]^{-1}dx \ , \quad (2)$$

and $\hbar\omega'=\hbar\omega-E_g'$ with E_g' containing the electron-hole exchange and correlation effects. Two independent fitting parameters were used, the plasma density and its effective temperature. A typical fit for the $x=0.001$ material is shown in Fig. 3. Except for a slight deviation on the low-energy tail (discussed below), there is excellent agreement between the calculated and the experimental results. In Fig. 4 we have plotted the renormalized band gap E_g', obtained from the above analysis, as a function of the plasma density and compared it with the prediction by a theoretical model recently published by Vashishta and Kalia.[12] The very good agreement between the theory and our experimental points lends strength to and provides an independent confirmation for our method of data analysis.

The values for plasma density obtained by this approach are plotted as a function of excitation intensity in Fig. 5. As can be seen, the density converges to a value of $n=6.5\times10^{17}$ cm^{-3}. Indeed, this value coincides very well with the equilibrium density of an EHL expected in ZnTe as calculated by Beni and Rice.[13]

In recent literature there are differing points of view concerning the existence of an EHL in a direct-gap semiconductor. This is in contrast to indirect-gap materials where the presence of an EHL has been thoroughly documented. The question, in a direct-gap semiconductor, is in part whether an EHL-like quasiequilibrium state can be established within the relatively short lifetime of the photoexcited carriers. Additionally, it has been pointed out how the experimentally observed "saturation" in the plasma density could also result from the expansion of an EHP caused by the large Fermi pressures which can accompany spatially inhomogeneous excitation. Such expansion has now been verified by observation in a number of direct band-gap semiconductors.[14] On the other hand, we expect a distinctly different signature for temperature dependence of the density in the case of an EHL and that of an expanding plasma. The density of an EHL should decrease with increasing temperature,[15] while the density of an expanding plasma has been found to increase with increasing temperature.[16]

For the case of ZnMnTe ($x=0.001$) we observe that the plasma density saturates also with increasing (effective)

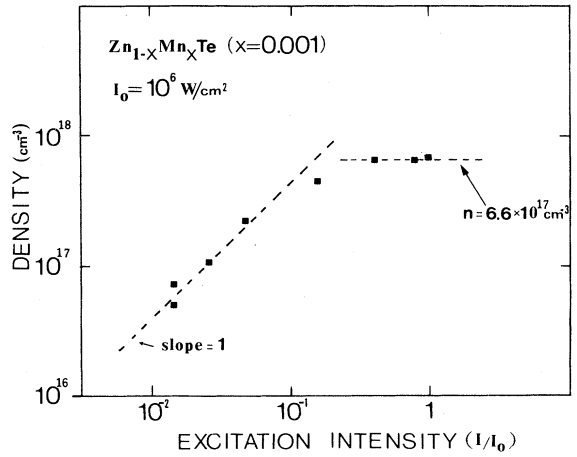

FIG. 5. Plasma density [as obtained from fitting the EHP emission to Eq. (1)] vs excitation intensity for the $x=0.001$ sample. Dashed lines represent linear variation of the density vs intensity and the $n=6.6\times10^{17}$ cm^{-3} value, which is the predicted EHL density for ZnTe (Ref. 13).

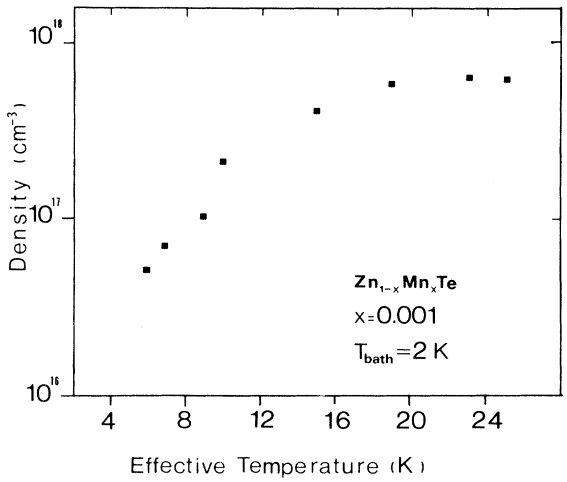

FIG. 6. EHP density vs effective plasma temperature for the $x=0.001$ sample. Both the density and the effective temperature values are obtained from the best fit to the EHP emission.

plasma temperature as shown in Fig. 6. This fact, together with the excellent agreement with the theoretically predicted equilibrium density provides us with strong evidence that the observed plasma emission is originating from an EHL. Measured from the free exciton energy, we find the binding energy for the EHL to be 11 meV, larger than the theoretical value.[13] The cause of an increase in the binding energy in this instance is presently unclear, although we note again the possibility for the exchange interaction by the Mn ions to stabilize the liquid. No theoretical estimates appear to have been made concerning the role for such an enhancement.

When pursuing the above analysis for the spectra obtained from samples of higher concentration of Mn, discrepancies with the simple line-shape model of Eq. (1) are encountered on the low-energy side of the emission band. In particular the departure from the theoretical line shape suggests an extension of the density of states below the parabolic band gap, behavior which was also confirmed by studying the fundamental edge absorption in our samples.[17] Such "band tails" are frequently encountered when dealing with the lowest interband resonances in mixed crystals and can be attributed to alloy potential fluctuations. In connection with line-shape analysis of an EHP and EHL, a somewhat analogous (though less serious) problem has been encountered previously, e.g., in Ge where linewidth broadening has been successfully accounted for due to an Auger process in the final state of the radiative transition.[18] In mixed crystals the severity of the problem has been recognized previously,[19] but to our knowledge no attempts to analyze the fluctuation broadened low-energy tail of an EHP luminescence band has been published so far. In the following we shall describe a simple model which we use to calculate the EHP line shape in $Zn_{1-x}Mn_xTe$ ($x=0.011$ and 0.016) by explicitly considering the effect of statistical compositional fluctuations on an otherwise intrinsically perfect crystal.

An approximation for the inherent band-edge broadening in a mixed crystal can be obtained by taking the view that the photoexcited carriers "feel" the crystal potential only within a characteristic volume V_0. In this volume the statistical fluctuations of the composition about a mean value x_0 can be described by a Gaussian distribution[20]

$$P(x')=be^{-(x'-x_0)^2/\rho^2}, \tag{3}$$

where b is a normalization constant. Since the energy gap in $Zn_{1-x}Mn_xTe$ is to a good approximation a linear function of composition for the range of interest here, we then account for the fluctuations by allowing the gap also to follow a Gaussian distribution about a mean value E_g^0,

$$P(E_g')=Ce^{-(E_g'-E_g^0)^2/E_0^2}, \tag{4}$$

where

$$E_0=\left|\frac{dE_g}{dx}\right|\left[\frac{x(1-x)}{V_0/v}\right]^{1/2}, \tag{5}$$

V_0 is the effective (local) volume and v is the volume of the unit cell.

We now construct a line shape for the EHP luminescence by an appropriate summation over the distribution of values for the energy gap. Formally, the line shape will be given by integration of the "unperturbed" EHP spectra [Eq. (1)], multiplied by the Gaussian weighing function

$$\begin{aligned} I(\hbar\omega)&=I_0\int_0^\infty dE_g' \exp-[(E_g'-E_g^0)^2/E_0^2]I(\hbar\omega,E_g') \\ &=I_0'\int_0^\infty dE_g' \exp\{-[(E_g'-E_g^0)^2/E_0^2]\}\int_0^{\hbar\omega'} dE\,E^{1/2}(\hbar\omega'-E)^{1/2}\{1+\exp[(E-E_F^h)/kT]^{-1}\} \\ &\quad\times\{1+\exp[(\hbar\omega'-E-E_F^e)/kT]\}^{-1}. \end{aligned} \tag{6}$$

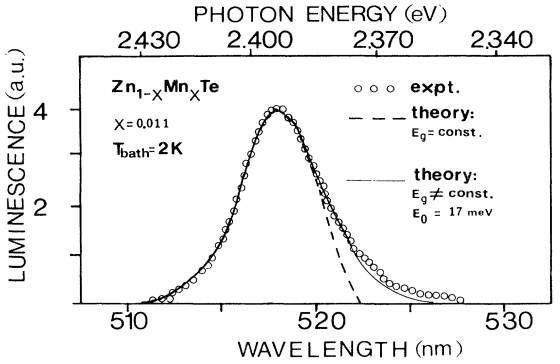

FIG. 7. EHP luminescence of $Zn_{1-x}Mn_xTe$ ($x=0.011$) vs photon energy. Dashed line represents the best fit using Eq. (1), while the solid curve takes the alloy potential fluctuations into account (see text).

We note also that due to the local fluctuations in the band gap, the plasma density will also fluctuate in this description of a mixed crystal. This follows since the chemical potential stays constant, i.e.,

$$\mu(n,T)=E_g'+E_F'^{e}+E_F'^{h}=\text{const}\ ,$$
$$n(E_F')=a\int_0^{\infty}x^{1/2}\exp[(x-E_F'/kT)+1]^{-1}dx\ . \tag{7}$$

We have used Eqs. (6) and (7) to fit our experimental results for the $x=0.011$ and 0.016 samples with E_0 used as an additional parameter. As can be seen by comparing theory with experiment in Fig. 7, excellent agreement can be reached by this approach. (The small mismatch on the low-energy tail is probably due to LO-phonon replica of the EHP band.)

The broadening parameter E_0 introduced above is directly connected to the characteristic "fluctuation volume" V_0 through Eq. (5). An effective length R can thus be defined as

$$R=\left[\frac{3x(1-x)}{4\pi E_0^2}\left[\frac{dE_g}{dx}\right]^2 v\right]^{1/3}\ . \tag{8}$$

Physically it is appropriate to approximate this length by the Fermi-Thomas screening length λ_{FT} given by

$$\left[\frac{1}{\lambda_{FT}}\right]^2=\frac{6\pi ne^2}{\epsilon E_F}\ , \tag{9}$$

where ϵ stands for permittivity. (In keeping with the approximate nature of this approach we have simplified the electron-hole screening by using this standard expression.) In Table I we summarize the observed dependence of E_0 on the excitation intensity, together with the plasma density, the calculated characteristic length R, and the Fermi-Thomas screening length λ_{FT}. The satisfactory agreement between the characteristic length R deduced from the experiments and the Thomas-Fermi screening length appears to justify the model used.

The plasma density obtained by the above analysis for the $x=0.011$ and 0.016 samples does not show any saturation effects, in contrast to the case for the $x=0.001$ composition. While this could be a consequence of several effects, we consider a reduction in the electron-hole lifetime in the samples of higher Mn concentration be a primary candidate for frustration of an EHL formation. A significant shortening of the lifetime was indirectly verified in our experiments for the samples of higher alloy fraction by comparing the amplitudes of the luminescent signals. Elsewhere, time-resolved luminescence studies in comparable semimagnetic semiconductors (CdMnTe) indicate that such a lifetime shortening accompanies higher alloy fractions.[21] Other contributions from alloy potential fluctuations may further explain why we would observe the EHL formation only in very dilute ZnMnTe ($x=0.001$). (In pure ZnTe EHL formation has been reported,[22] although contrary evidence has also been presented.[23])

TABLE I. Comparison of the excitation (density-) dependent characteristic length R as calculated from the measured energy broadening parameter E_0, with the Fermi-Thomas screening length λ_{FT}. The values used in the calculation were $1/m^*$ (reduced effective mass)$=1/m_e+1/m_h=0.094$ (Ref. 24), ϵ (dielectric constant)$=10.1$ (Ref. 24), $dE_g/dx=2.5$ eV (from our measurements), and v (volume of primitive cell)$=5.6\times10^{-23}$ cm^3 (Ref. 24).

I/I_0	N (cm^{-3})	E_0 (meV) ($x=0.011$)	R (Å)	λ_{FT} (Å)
1	5×10^{17}	17	14.7	12.3
0.8	4.5×10^{17}	16	15.3	12.5
0.5	3×10^{17}	12	18.6	13.4
0.2	1×10^{17}	7	26.6	16.1
		($x=0.016$)		
1	5×10^{17}	18	16.0	12.3
0.8	4.5×10^{17}	17	16.6	12.5
0.5	2×10^{17}	16	17.3	14.4
0.2	0.8×10^{17}	9	25.4	16.7

III. SUMMARY

We have presented results of experimental work where photoluminescence in the semimagnetic (Zn,Mn)Te has been studied for three alloy compositions under low and high intensity of excitation. We find first that the bound-exciton binding energy is composition dependent, attributed mainly to an exchange-induced contribution by the paramagnetic Mn ions. Second, line-shape analysis of the EHP emission for the $x=0.001$ material yields plasma parameters which are consistent with the formation of an EHL at a critical density of 6.5×10^{17} cm^{-3}, as also predicted by theory. In contrast, the samples with higher alloy fraction do not show evidence for such liquid formation in the same range of excitation intensities, possibly due to detrimental electron-hole lifetime effects. Finally, in our analysis of the EHP parameters for $x=0.011$ and 0.016 materials, we have introduced a simple model which has been used to obtain good agreement with observed spectra while taking alloy compositional fluctuation into account.

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