Excitonic Mobility Edge in $GaAs_xP_{1-x}$

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(Received 22 October 1985)

Time-resolved, selectively excited fluorescence and resonant Raman scattering (RRS) are used to determine the nature of excitons in $GaAs_xP_{1-x}$ ($x \leq 0.07$). All localized excitons, both intrinsic and those bound to isoelectronic nitrogen impurities, have the same e-h exchange splitting into $J=1,2$ levels. This allows measurement of the density of terminal states and their contribution to RRS by zone-edge LO_X phonons. An abrupt vanishing of the density of terminal states and this RRS presents firm evidence of the existence of an excitonic mobility edge and determines its position to an accuracy of 1 meV.

PACS numbers: 71.35.+z, 71.50.+t, 78.55.Ds

The lowest energy, $1S$ exciton band in mixed semiconductors, such as $GaAs_xP_{1-x}$, is perturbed by potential fluctuations which are due to local composition fluctuations. The resulting density of states is an approximately exponential tail for intrinsic excitons[1,2] and a Gaussian band for those bound to impurities[3] (Fig. 1). Exciton dynamics, which involves energy relaxation within these bands, has been studied by fluorescence-line-narrowing and spectral-diffusion experiments.[4] A central experimental problem is the determination of an excitonic mobility edge (marked ME in Fig. 1), namely, the demarcation energy between localized and extended states. The above-mentioned experiments are insufficient because just below ME, the inverse transfer rate can be shorter than the experimental time resolution. Indeed, subnanosecond time-resolved spectroscopy of selectively excited fluorescence in $CdS_{0.53}Se_{0.47}$ could not accurately determine the ME position.[5] Hegarty *et al.*[6] have used this technique and resonant Rayleigh scattering to show that a ME exists in semiconductor quantum wells.

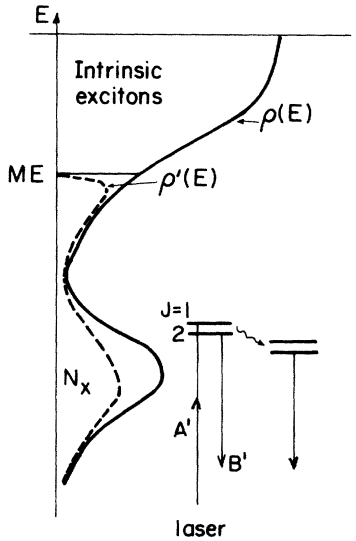

FIG. 1. A schematic representation of the excitonic states and processes in the alloy semiconductor system $GaAs_xP_{1-x}$. $\rho(E)$ is the density of all excitonic states, both intrinsic and bound to nitrogen impurities. $\rho'(E)$ is the density of terminal states. For localized states selective laser excitation (A' line) is followed either by relaxation and subsequent emission (B' line) or by phonon-assisted tunneling.

In the present study we combine the results of fluorescence-line-narrowing, spectral-diffusion, and resonant-Raman-scattering (RRS) experiments in order to determine the nature of intrinsic $1S$ exciton states in nominally undoped and nitrogen-doped $GaAs_xP_{1-x}$. We show that the well-known electron-hole exchange splitting of the N-bound exciton in GaP is also observed for localized excitons in $GaAs_xP_{1-x}$, both intrinsic and N bound. We schematically show this splitting for two subsets of localized excitons in Fig. 1. The different symmetry of the resulting $J=1$ and $J=2$ levels and the recently measured[7] relaxation rate between them (50 psec at 2 K for N-bound excitons in GaP) make this system most suitable for studying exciton dynamics. Since excitation is only into the $J=1$ level (A' line), it can be followed either by relaxation into the lower $J=2$ level and subsequent emission (B' line) for terminal states, or by phonon-assisted tunneling into other localized excitons (Fig. 1). This allows one to measure directly the density of terminal states $\rho'(E)$, namely, the subset of localized excitons which recombine radiatively before they can tunnel (at $T=0$).[8] Using time-resolved spectroscopy, we separate the RRS from background fluorescence and thus are able to observe scattering by zone-edge LO_X phonons. This scattering is forbidden by momentum conservation for free excitons but is induced by those in localized states. These experiments provide a new way to confirm the existence of a real excitonic

ME and accurately determine its energy position within the exciton band tail.

The crystals studied were all bulk, indirect-gap $GaAs_xP_{1-x}$. They were either nominally undoped (but containing background nitrogen impurities at an estimated concentration of 10^{15} cm^{-3}) or nitrogen doped to a level of about 10^{17} cm^{-3}. The excitation source was a dye laser which operated either cw or in a cavity-dumped mode with a pulse width of 7 nsec. The laser linewidth was 0.12 Å and the maximum intensity impinging on the sample was 0.1 W/cm^2. The spectra were monitored with a double monochromator having a resolution of 0.05 Å. They were analyzed with a photon-counting system, which could be gated for pulse work, with a resolution determined by the laser pulse width. We shall report here only the $T=2$ K results for samples with $x \leq 0.07$.

Figure 2 presents the results of a spectroscopic study of a nominally undoped $GaAs_{0.07}P_{0.93}$ crystal. Fluorescence and RRS spectra are shown for several excitation energies (marked l in the figure). In Figs. 2(a) and 2(b) the prominent features are the intense band (marked N_x) due to the recombination of N-bound excitons and its phonon sidebands.[9] Near the laser line, weaker features are observed. A sharp line (denoted B') is observed only for excitation energies below 2.314 eV (marked ME in Fig. 2). In the range of 2.290–2.314 eV the B' line is too weak to be resolved from the scattered laser line. Therefore, a magnetic field of 28 kG was applied and the lowest component of the Zeeman-split B' line could be observed under cross polarization, at 1.3 meV below the laser line.[10] For excitation within the N_x band [below ~ 2.290 eV, Fig. 2(c)], the B' line is about 2 orders of magnitude more intense, and is observed at 0.8 meV below the laser line. Under an applied magnetic field it shows a Zeeman splitting which is identical to that of the low-energy components ($m_J=0, -2$) of the $J=2$ level of excitons bound to nitrogen in GaP.[10] The other observed spectral feature is a band peaking about 3.2 meV below the exciting laser line [marked *FF* in Figs. 2(a) and 2(b)] which is due to acoustic-phonon-assisted tunneling between localized exciton states.[4] All those fluorescence lines and bands have a long lifetime (~ 300 nsec). The lines corresponding to emission which involves optical phonons (shifted by the energies of TO_Γ, LO_X, and LO_Γ phonons from the exciting laser line) have been observed in the pulse mode. The gate was set coincident with the laser pulse as these lines were found to have a prompt response. They are thus identified as Raman lines. The RRS by LO_X phonons was observed only for excitation energies below ME. The relative intensities of both the B' line and the LO_X Raman line, normalized to their peak intensities, as functions of excitation energy are shown in Fig. 2(d). The same figure also shows the transmission spectrum. It exhibits a weak N_x band and a tail of absorption due to intrinsic excitons. A similar study was done on a N-doped $GaAs_{0.02}P_{0.98}$ crystal. For excitation energies above 2.312 eV (marked ME in Fig. 3), spectra such as that shown in Fig. 3(a) are observed while Fig. 3(c) shows a typical spectrum for excitation below the ME. The transmission spectrum and the fluorescence spectrum excited high in the exciton band are shown in Fig. 3(b).

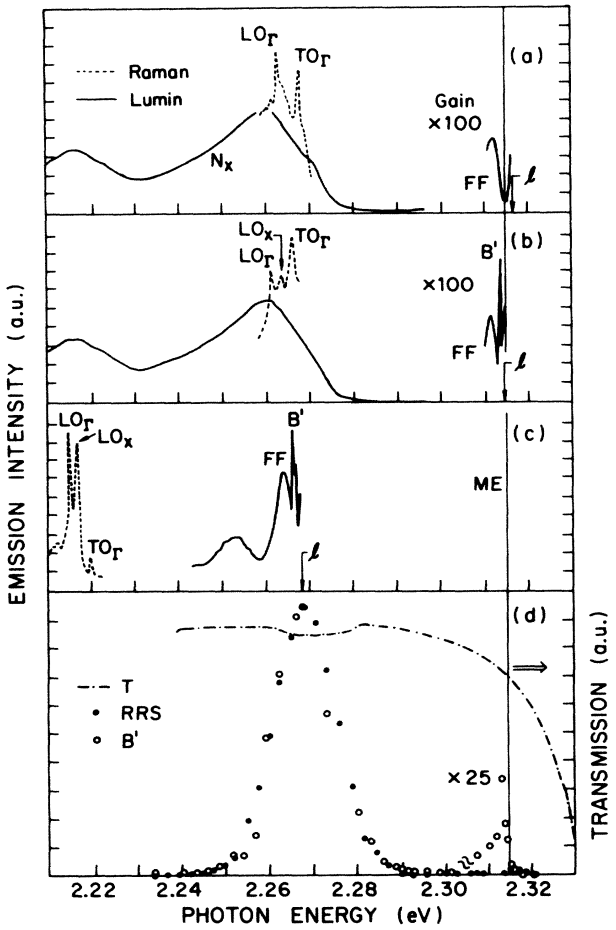

FIG. 2. (a) cw luminescence spectrum excited just above the ME. The RRS by optical phonons is observed in the pulse mode. (b) Same as in (a) but excited just below the ME. The line marked B' is observed under an applied magnetic field of 28 kG. (c) Same as in (b) but excited within the N_x band. (d) Transmission spectrum of $GaAs_{0.07}P_{0.93}$ showing the N_x band and the tail of absorption due to intrinsic excitons. Also shown are the intensity of the B' line (or its lowest Zeeman component) and of the LO_X RRS line for various laser excitation energies.

We interpret the observations for both crystals in terms of the dynamics of excitons subjected to potential fluctuations of the disordered semiconductor. The essentials of the model are as follows: There are two types of intrinsic excitons, extended and localized,

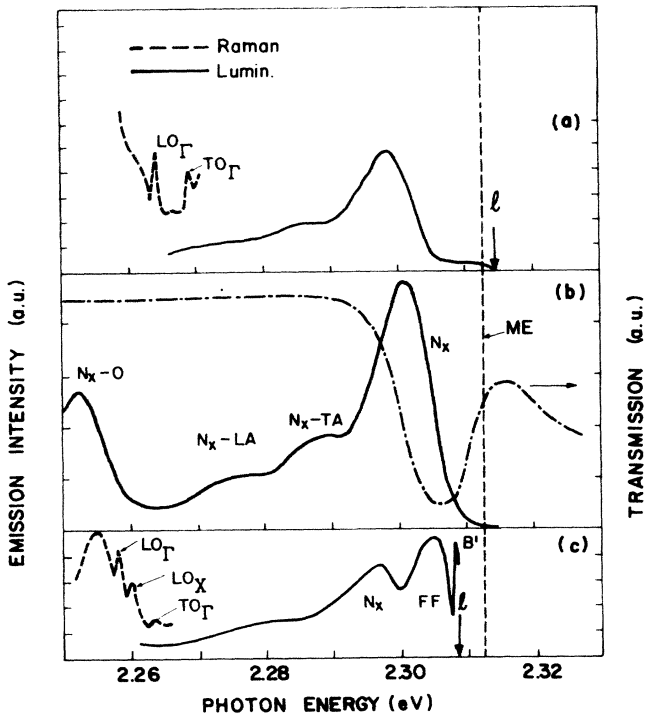

FIG. 3. (a) Luminescence spectrum excited just above the ME. The RRS by optical phonons is observed in the pulse mode. (b) Transmission and luminescence spectra. The latter was excited at 2.333 eV. (c) Same as in (b) but excited within the N_x band.

which are separated in energy by a sharp mobility edge. The density of exciton states bound to nitrogen impurities overlaps that of intrinsic excitons to an extent which depends on the crystal composition. These can be localized or extended according to the ME energy with respect to the N_x band. Localized excitons can spatially diffuse by tunneling until they reach a terminal state where they recombine. Localized excitons, bound either to nitrogen impurities or to intrinsic potential fluctuations, have the same e-h exchange splitting into $J=1,2$ levels with subsequent Zeeman splitting as those in GaP:N. The density of terminal states, $\rho'(E)$, is measured by the excitation energy dependence of the B' line intensity. $\rho'(E)$ vanishes abruptly at the ME. The localized exciton states contribute most strongly to the RRS involving LO_X phonons, because a localizing potential contains Fourier components with zone-edge wave vectors. Extended states do not contribute to this RRS since their wave function averages out short-range potential fluctuations. The abrupt disappearance of the LO_X RRS spectrum thus provides an additional verification of the existence of a ME.

Consider the undoped $GaAs_{0.07}P_{0.93}$ crystal, in which case the N_X band is well separated from the band of intrinsic excitons. Selective excitation within this band is into the $J=1$ level (the A' line which is dipole allowed) of a resonant subgroup of exciton states. Some of these states are terminal, and the exciton relaxes into the $J=2$ level where it recombines radiatively. This gives rise to the B' line, which is dipole forbidden and thus has a long lifetime (as in GaP:N). Therefore the dependence of the B' intensity on excitation energy E provides a direct measure of the (relative) density of terminal states. This $\rho'(E)$ can be followed along the wings of the N_x band. In the higher energy range ($E > 2.290$ eV) the density $\rho(E)$ of intrinsic exciton states is increasing with E, as can be seen from the absorption spectrum [Fig. 2(d)]. The B' line is observed in this range through its lowest Zeeman component which has an identical energy shift from the laser line as that observed in GaP:N. This means that intrinsic excitons which are localized by potential fluctuations have the same exchange splitting as those bound to nitrogen impurities. The abrupt vanishing of the B' line intensity at the ME is interpreted as follows: Above the ME, excitons are created in their $J=1$ level. Being extended, their trapping rate by any localized state is much higher than the $J=1 \rightarrow J=2$ relaxation rate. It should be noted that the ME is located high in the tail of the intrinsic exciton band (about 40 meV above the N_x peak). Lai and Klein[11] have observed fluorescence of intrinsic excitons in $GaAs_xP_{1-x}$ with $x \geq 0.14$. However, their experiments allowed the observation of the lowest-energy part of the intrinsic-exciton spectrum only, while here we observe the spectrum of terminal states all the way up to the ME.

The LO_X RRS intensity is also determined by $\rho'(E)$ in the following way. As argued above, only localized states can induce the RRS by zone-edge phonons. Since there is a single resonance at the $J=1$ level of each localized exciton, we can approximate the LO_X RRS spectrum by the following expression[12]:

$$I(E_l) = C \int dE \int d\Gamma \frac{\Gamma \rho(\Gamma, E)}{(E-E_l)^2+\Gamma^2}, \tag{1}$$

where E_l is the laser energy and C contains all the exciton-phonon and exciton-photon interaction matrix elements, which are assumed to have the same value for all $1S$ excitons. For a given exciton energy E, there is a distribution of dephasing rates, Γ, of the $J=1$ level. These depend on the tunneling probability of the various localized excitons. Clearly, large contributions to $I(E)$ come from small values of Γ. The smallest Γ is equal to the inverse $J=1 \rightarrow J=2$ relaxation time: $\Gamma_{\min} \sim 0.03$ meV.[7] This is the case for terminal states and thus $\rho(\Gamma_{\min}, E) = \rho'(E)$. Then we have

$$I(E_l) \propto \int dE \frac{\Gamma_{\min} \rho'(E)}{(E-E_l)^2+\Gamma_{\min}^2} \propto \rho'(E_l), \tag{2}$$

since, for this small $\Gamma_{\min}$, the Lorentzian term in the

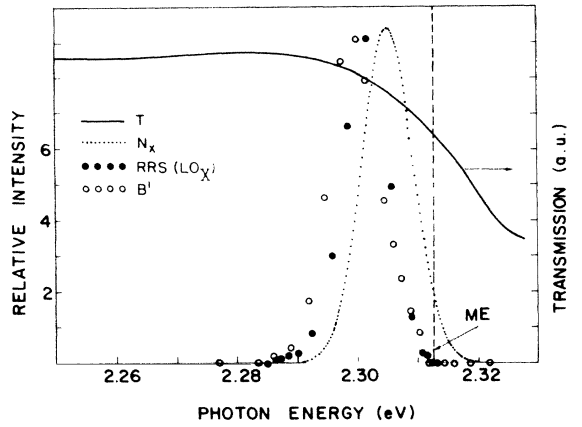

FIG. 4. The intensity of the B' line and of the LO_X RRS line for various laser excitation energies (extracted from data such as in Fig. 3 for $GaAs_{0.02}P_{0.98}$:N). Also shown are the Gaussian density of N-bound exciton states and the transmission spectrum due to intrinsic excitons.

integrand is essentially a δ function. Figure 2(d) shows that the LO_X RRS spectrum is proportional to $\rho'(E)$ to a very good approximation in the energy range of N-bound excitons. At higher excitation energies, the LO_X RRS is weak and thus a quantitative comparison with $\rho'(E)$ is difficult. However, it clearly vanishes at the ME [cf. Figs. 2(a) and 2(b)]. This provides further support to the identification of the ME.

The case of the nitrogen-doped $GaAs_{0.02}P_{0.98}$ crystal is somewhat more complex since the N_x band overlaps the tail of intrinsic exciton absorption. We have therefore separated these two by first fitting a Gaussian curve to the N_x absorption and then subtracting it from the experimental curve. The results are shown in Fig. 4, and they provide a measure of the density of states of N-bound and intrinsic excitons. $\rho'(E)$ is again determined by the B' line intensity dependence on the excitation energy E. It vanishes at 2.312 eV (marked ME in Fig. 4), which is well within the N_x band. The LO_X RRS intensity vanishes at the same energy. If the N_x band were completely separated from the band tail of intrinsic excitons, then all the N-related exciton states would have been localized, and a behavior similar to that described for $x=0.07$ would have been observed. It is thus the overlap of N_x with the band of intrinsic excitons that changes the nature of N-related excitons: For E above the ME, they are resonant with extended excitons.

In summary, we have resolved the internal splitting of the $1S$ exciton localized by either the isoelectronic N impurities or the intrinsic potential fluctuations. The relaxation between the $J=1$ and $J=2$ levels competes with various transfer processes of the exciton as a whole. This results in a B' line for terminal states and a phonon-assisted transfer band. In addition we have shown that the terminal exciton states induce RRS by LO_X phonons. Using these experiments we were able to determine the position of the excitonic mobility edge in $GaAs_xP_{1-x}$ ($x \leq 0.07$). An interesting problem that remains to be dealt with is the relation between the position of the mobility edge and the degree of disorder, which in turn is related to the composition parameter.

This study was supported by the United States–Israel Binational Science Foundation.

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