Donor states in GaAs under hydrostatic pressure

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Spectroscopic studies have been carried out for GaAs crystals under hydrostatic pressure, intended for the investigation of effective-mass donor levels associated with different conduction-band minima and the *DX* center. Our results reveal the existence of three donor states appearing in the band gap. These are labeled D_Γ, D^*, and D_X. The donor state D_Γ, normally observed at atmospheric pressure, successively crosses two other donor states (D^* and D_X) as the hydrostatic pressure exceeds 28 kbar. D^*, in turn, crosses D_X at pressures of about 44 kbar. From their corresponding donor-acceptor pair luminescence, we know that D_Γ and D_X have pressure dependences that track the Γ- and X-band minimum, and are believed to be effective-mass donor states associated with the Γ- and X-band edges, respectively. The third donor state D^* has a pressure dependence that does not seem to agree with any known conduction-band minimum. However, it is in many respects similar to the *DX* center, although it has not, in studies of radiative emission, revealed evidence of a large lattice relaxation and photoquenching effects.

I. INTRODUCTION

Substitutional donor dopants appearing on both the group-III sites (Ge, Si, Sn) and the group-V sites (S, Se, Te) in GaAs and related alloys have received increasing attention in recent years. This is because the electrical conduction processes in these materials are found to be controlled by a defect which can either act as a deep donor or as an effective-mass donor,[1-5] with a complicated interplay between these two states. The peculiar deep-donor state, which is known as the *DX* center, is believed to affect the performance of modulation-doped field-effect transistors (MODFET's) made of $Al_xGa_{1-x}As/GaAs$, the structure of a device employed in high-speed digital and analog circuits.[6,7] A special manifestation of the *DX* center is the appearance of slow transients in the switching characteristics of MODFET's.[8]

The *DX* center in $Al_xGa_{1-x}As$ alloys for $x > 0.22$ has the unusual properties of persistent photoconductivity (PPC) at low temperatures[9,10] resulting from large barriers for thermal capture and emission into and out of the deep states,[1,2] and a large threshold for photoionization compared with thermal ionization.[1,2] These properties led Lang *et al.*[1,2] to propose a process of multiphonon capture and emission and a large lattice relaxation upon the capture of a charge by the defect. A donor complex *DX* consisting of a simple donor (D) and an unknown defect (X) was postulated. However, the following facts, discovered later, provide evidence that the *DX* center arises from an isolated donor atom alone. (1) All the donor atoms incorporated into the crystals are electrically active as *DX* centers,[11] independent of the technique used for crystal growth. (2) Donors of different species have qualitatively similar effects.[12] (3) The *DX* center is also present in GaAs (Refs. 13–15) and it becomes the state of the lowest energy when the pressure exceeds about 24 kbar. The number of the *DX* defects thus created equals the number of charge carriers to within a small factor. (4) The studies on local vibrational modes in GaAs:Si indicate that it seems unlikely for the majority of Si donors in GaAs to form complexes.[16] These have led to suggestions that the *DX* center involves a substitutional donor atom with small[17,18] or a displaced donor atom with large[19-22] lattice relaxation. A recent proposal[23,24] is that the *DX* center is a displaced donor which has a two-electron negative-U D^- state. A large lattice relaxation energy for the *DX* center is required in this new model.

At the present time the great majority of experimental results favors the *DX* center with a large lattice relaxation. However, in spite of extensive study, the physics of the *DX* center remains controversial. In this work, we study the donors in GaAs under hydrostatic pressure by all-optical methods, which are motivated by the following.

(i) Theoretically, the existence of secondary extrema in the band structure may produce additional bound and resonant states.[25] There is a challenge for experimental investigations of these states associated with each of the conduction-band minima introduced by donorlike impurities in GaAs.

(ii) It seems well established that the *DX* center is intimately linked to the poorly understood, localized, resonant donor levels in GaAs or $Al_xGa_{1-x}As$ alloys.[13-15,26] Applying hydrostatic pressure to GaAs modifies the conduction-band structure in much the same way as increasing the Al composition does.

(iii) Among the studies on *DX*, few employ all-optical methods. Photoluminescence (PL) results[18] attributed to the *DX* center in $Al_xGa_{1-x}As$ alloys with a model of small lattice distortion are currently a subject of debate.

(iv) Pressure has an advantage over changing the composition of the alloy in that variations in the properties of the defect due to different sample histories and effects of alloy fluctuations can be avoided. A pure band-structure

effect will thus be obtained by applying hydrostatic pressure. In addition, the spectra from pressure measurements can be traced much more easily than those in the corresponding alloy experiment.

When the conduction-band structure in GaAs is continuously changed by the application of hydrostatic pressure, resonant donor levels related to higher conduction-band edges as well as deep states may be pushed into the forbidden gap and act as radiative centers.[27,28] Based on the observation of the DX center in GaAs under hydrostatic pressure [by deep-level transient spectroscopy (DLTS)], much attention has in the present study been paid to the pressure region at which the DX level is expected to appear in the band gap. At a pressure of about 28 kbar, a new, deep, donor-acceptor peak (D^*A) starts to be observable and soon becomes the lowest-energy donor-acceptor (DA) peak in the PL spectrum and a dominant recombination level. D^* is proposed to be related to the DX center, since our investigation of D^*A shows that it behaves in many respects like the luminescence related to the DX center. Another donor-acceptor peak, which is believed to be related to the effective-mass donor level associated with the X-band edge (D_X), appears in the recombination spectra at higher pressures. It crosses D^*A and becomes, in turn, the lowest-energy transition at and above 44 kbar.

The following presentation of this study is divided into four sections. Samples and experimental methods are first described in Sec. II. The experimental results and discussions are presented in Secs. III and IV, respectively. Finally, a summary is given in Sec. V.

II. SAMPLES AND EXPERIMENTAL METHODS

GaAs crystals doped with different donors, S, Si, Te, were grown by liquid-phase epitaxy (LPE) or metalorganic vapor-phase epitaxy (MOVPE). The epitaxial layer thicknesses were typically 3 μm. The best samples for our investigation are those with donor concentration in the order of $10^{15}-10^{16}$ cm^{-3}. The concentration of unintentionally doped acceptor in a sample is not exactly known, a typical compensation level for the growth conditions used would suggest the concentration of the acceptor to be about $\frac{1}{3}$ of the donor concentration. The sample codoped with Cu and a shallow acceptor C was prepared by diffusion from an evaporated Cu film into liquid-encapsulated Czochralski (LEC) -grown GaAs which is unintentionally doped with C. The diffusion took place for 4 h at 750 °C. For the hydrostatic-pressure measurement, samples were mechanically lapped to a thickness of about 30 μm and then cleaved into about 100×100-μm dies. A suitable piece was loaded into a gasketed diamond-anvil cell (DAC) of the Merril-Basset type, and argon was used as the pressure-transmitting medium.

Low-temperature PL was measured in a forward-scattering geometry with the DAC immersed in liquid He pumped below the critical point. For excitation above the band gap, the 5145-Å emission from an Ar^+ laser was used as excitation source. For below band gap, selective excitation, or the measurement of PL excitation, the Ar^+ laser was used to pump a DCM [4-(dicyanomethylene)-2-methyl-6-(*p*-dimethyl-amino-styryl)-4*H*-pyran] dye laser from which tunable emission from wavelength 6300 to 7000 Å can be obtained. The signal was dispersed by a 0.75-focal-length double-grating monochromator and detected in a GaAs photomultiplier and a photocounting equipment. When time-resolved measurements were performed, an acousto-optic modulator was used to modulate the cw laser, resulting in laser pulses with a fall time of 10 ns. A gate signal (minimum width of 50 ns) from a boxcar was applied to the photon counter which allowed the signal to be counted only within the time of the gate. Luminescence spectra of different delay times, or time decay of the intensity of a transition, could thus be measured.

III. EXPERIMENTAL RESULTS

A. The observation of D^*A and D_XA

Figure 1 shows the low-temperature PL spectra of an S-doped GaAs sample at different hydrostatic pressures. A spectrum measured at atmospheric pressure [Fig. 1(a)] shows the well-understood, near-band-edge luminescence of GaAs. The donor-bound exciton recombination peak (D^0_Γ) lies on the highest-energy side, where D_Γ is the shallow, effective-mass donor state associated with the Γ conduction-band minimum. On the lower-energy side of D^0_Γ are the donor-acceptor recombination peak ($D_\Gamma A$) and its phonon replica ($D_\Gamma A$-LO). The acceptor involved is carbon. Free-to-bound transitions may have some contribution to the labeled $D_\Gamma A$ peak, but they are usually not important at liquid-helium temperature; only at temperatures higher than about 50 K do they begin to dominate the spectrum, when the shallow donors start to ionize. With increasing pressure, all the near-band-edge peaks move to higher energies at a rate of 10.73 meV/kbar (Ref. 29) as the GaAs band gap increases. The peaks can be very well traced. Changing the excitation power is always helpful in distinguishing these transitions. The luminescent intensity of D^0_Γ increases linearly (or superlinearly) with excitation, while the donor-acceptor (DA) transition shows an inhomogeneous saturation and a shift of the peak position to higher energy at a high excitation density.

At 28 kbar [Fig. 1(b)], a shoulder (D^*A) is observed on the higher-energy side of $D_\Gamma A$. D^*A is stronger if we increase the excitation intensity, as shown in the dashed-line spectrum in Fig. 1(b). The pressure coefficient of D^*A is much smaller than that of $D_\Gamma A$, and for slightly higher pressure it crosses to the low-energy side of $D_\Gamma A$ [Fig. 1(c) at 31 kbar]. While on the low-energy side of $D_\Gamma A$, D^*A is easily observed as the dominant, radiative, recombination channel at low excitation power.

A further increase in pressure [Fig. 1(d) at 34 kbar] reveals another peak, D_XA. This peak has a negative pressure coefficient. It moves to lower energies with increasing pressure and merges later into D^*A. While on the high-energy side of D^*A, D_XA is more easily observed at high excitation power [Fig. 1(e)]. The inset in Fig. 1 illustrates qualitatively the energy-level diagram proposed for

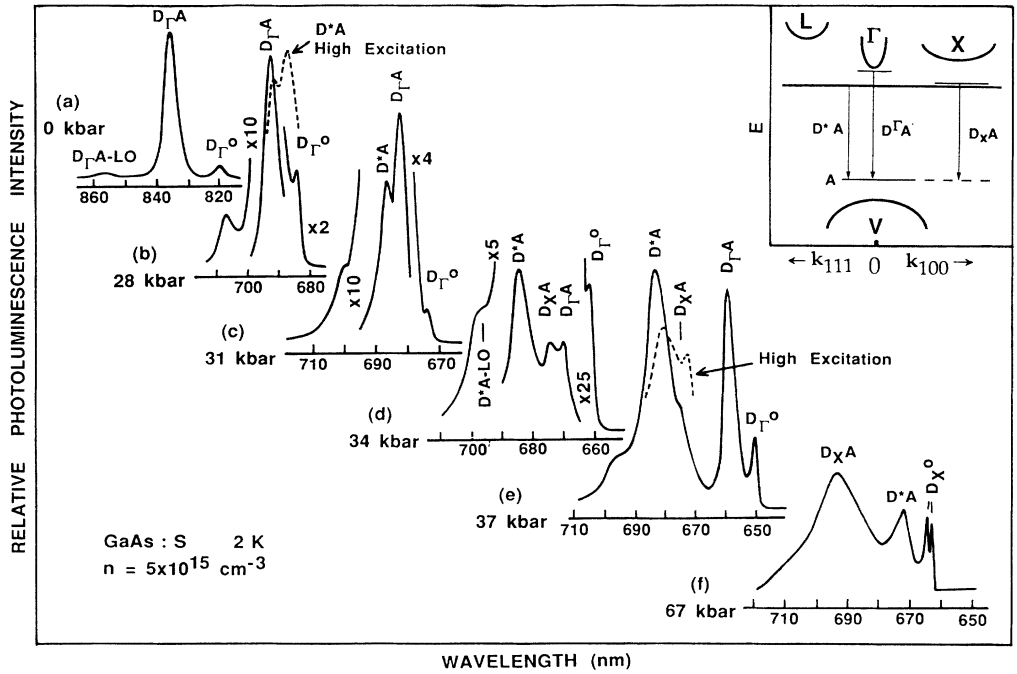

FIG. 1. PL spectra of an S-doped GaAs sample observed at different hydrostatic pressures. Below 28 kbar, the spectra observed are direct, near-band-edge luminescence normally seen at atmospheric pressure, consisting of donor-bound exciton luminescence D^0_Γ, donor-acceptor pair transition $D_\Gamma A$, and its phonon replica (a). They shift smoothly to higher energies with increasing pressure. For pressures above 28 kbar, two peaks D^*A and $D_X A$ cross $D_\Gamma A$ successively. With increasing pressure, D^*A moves to higher energies while $D_X A$ moves to lower energies. Dashed lines in (b) and (e) show the situations corresponding to higher excitation densities. The inset in the figure shows the energy-level diagram corresponding to the situation in spectrum (e), i.e., D^* has the lowest energy and D_Γ the highest energy.

the situation in the spectrum in Fig. 1(e), that is, $D_\Gamma A$ has the highest energy and D^*A has the lowest. As will be discussed below, D_Γ and D_X are drawn as donor states attached to the Γ- and X-band edges, respectively, while D^* is drawn as a deep donor with its electronic wave function delocalized over the whole Brillouin zone. Figure 1(f) shows that at 67 kbar, $D_X A$ has crossed D^*A and has the lowest recombination energy. At this pressure, the recombination of excitons bound to the donor state associated with the X-band edge (D^0_X) is also observed, and appears instead of D^0_Γ after the onset of the direct-indirect crossover of the GaAs band gap.[29]

B. Pressure dependence

The pressure dependences of donor-acceptor recombinations $D_\Gamma A$, D^*A, and $D_X A$ up to about 65 kbar are summarized in Fig. 2. Also illustrated are the pressure dependences of the X and L conduction-band minima. It can be seen that while $D_\Gamma A$ and $D_X A$ follow the Γ and X conduction-band minima, with pressure coefficients of 10.73 and -1.34 meV/kbar, respectively,[29–31] D^*A shows a pressure dependence of 1 meV/kbar. It does not seem to track any known conduction-band edge [the L conduction-band minimum has a pressure coefficient of about 5.5 meV/kbar (Refs. 30–32)]. Since the effect of hydrostatic pressure on acceptor energy levels is negligible, the observed pressure dependences of the DA peaks are therefore those of donor energy levels. These findings thus suggest that we are observing donor states associated with the Γ- and X-band edge, and a deep-donor state D^*.

It can be seen from Fig. 2 that $D_\Gamma A$ has the lowest recombination energy below 28 kbar. It crosses D^*A at 28 kbar, which then has the lowest recombination energy up to 44 kbar, at which $D_X A$ becomes the lowest-energy peak.

C. Observations in different samples

The new peaks at pressures higher than a critical value have been observed in different types of samples. The results of GaAs epitaxial samples doped with different donors and bulk material codoped with two acceptors are presented in this section.

It seems that for any choice of donor in GaAs, the splitting appears when the pressure exceeds a critical value. It does not make much difference whether it is an n- or p-type material or whether it is high-quality epitaxial layers or bulk materials. However, it seems that the splittings are most favorably observed for well-compensated samples with a donor concentration in the order of 10^{15}–10^{16} cm^{-3}. Such a sample would show a D^0_Γ peak of moderate intensity and a sharp and strong $D_\Gamma A$ peak. A compensated sample with a high donor

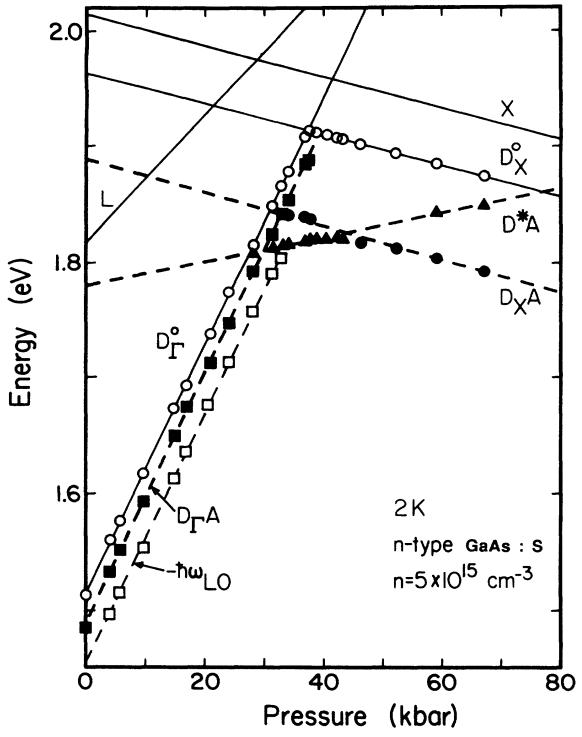

FIG. 2. Pressure dependence for the peaks observed in Fig. 1. $D_\Gamma A$ and $D_X A$ have about the same pressure coefficients as the Γ- and X-band edges, namely 10.73 and -1.34 meV/kbar, respectively. D^*A, however, shifts to higher energies at a rate of about 1 meV/kbar, which does not track any known conduction-band minimum. The first crossing, of $D_\Gamma A$ and D^*A, occurs at 28 kbar. The second crossing, of D^*A and $D_X A$, occurs at about 44 kbar. D^0_Γ and D^0_X are the direct (Γ) and indirect (X) donor-bound exciton emissions, respectively.

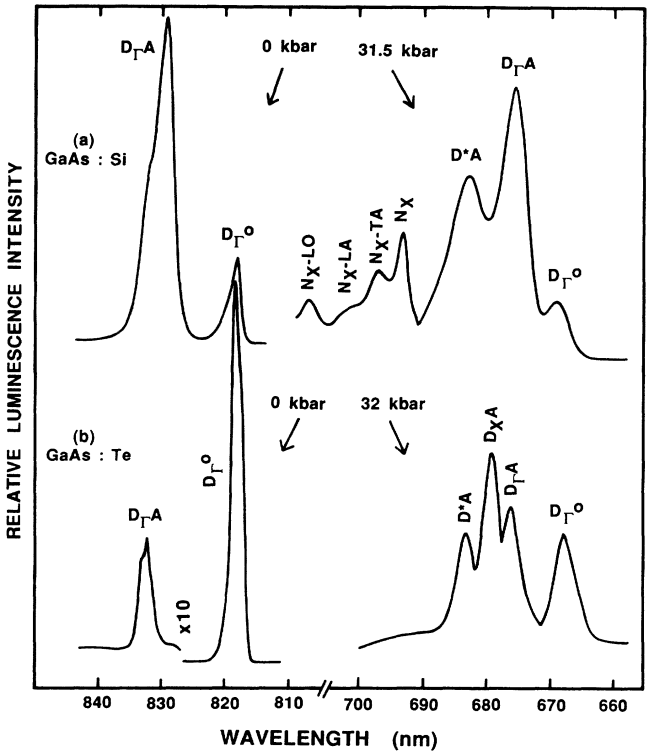

FIG. 3. Spectra of (a) GaAs:Si and (b) GaAs:Te at atmospheric pressure and pressure higher than the critical value, which illustrates the observations of splittings in these samples. The observation of bound exciton luminescence due to isolated nitrogen inadvertently introduced and its phonon replicas in the GaAs:Si sample at 31.5 kbar are also demonstrated in (a).

concentration shows a broad donor-acceptor recombination peak, which gives rise to difficulties in resolving the peaks. A sample with a too small donor or acceptor concentration shows a much weaker donor-acceptor recombination compared with donor-bound exciton recombination (D^0_Γ), resulting instead in the difficulty of investigating the splitting of the DA recombination and hence the splitting of the donor.

The phenomena observed in GaAs samples doped with Si and Te are illustrated in Fig. 3. At atmospheric pressure, their spectra are all similar to the S-doped sample. They consist of D^0_Γ and $D_\Gamma A$. At higher pressures, they also show splittings similar to those described in Sec. III A, although there are some minor differences in peak position and intensity. Spectra of GaAs:Si at 31.5 kbar and GaAs:Te at 32 kbar are illustrated. The identification of the peaks in Fig. 3 is not straightforward, since spectra at pressures near the splitting are complicated. In order to identify the peaks observed, one has to (i) carefully tune the pressure, (ii) follow the change of spectra from low to high pressures, and (iii) study the variation of the spectra at different densities of the excitation power.

It is worth remarking here that some samples in our study turn out to have an unexpected, strong luminescence from nitrogen-bound excitons. Although luminescence from excitons bound to nitrogen pairs[33] can only be observed in GaAs samples with fairly high nitrogen concentration, radiative recombination of excitons bound to isolated nitrogen atoms (N_x) is strong even in very weakly or unintentionally nitrogen-doped samples. N_x is observed at a pressure higher than 22 kbar. An example is given in Fig. 3(a) of our GaAs:Si crystal. No nitrogen is seen at atmospheric pressure, while at 31.5 kbar the N_x peak and its phonon replicas are quite strong.

It is important to identify in which of the states involved in the recombination the energy-level splitting occurs for critical pressures. For this purpose, a sample codoped with two different acceptors is investigated. Illustrated in Fig. 4 is a GaAs sample codoped with Cu and C investigated at low temperature. Cu in GaAs introduces a deeper acceptor energy level [155 meV (Refs. 34 and 35)] than does C [30 meV (Ref. 36)]. The donor-acceptor peaks in the PL spectra of such a sample show a simultaneous splitting under hydrostatic pressure. At low pressures [see 23 kbar in Fig. 4(a)], two $D_\Gamma A$ peaks are observed, one corresponding to the C acceptor ($D_\Gamma A_1$, A_1 is carbon), the other the Cu acceptor ($D_\Gamma A_2$, A_2 is copper). On the low-energy side of and separated by about 36 meV from these $D_\Gamma A$ peaks are their LO^Γ phonon replicas. With increasing pressure, they all move

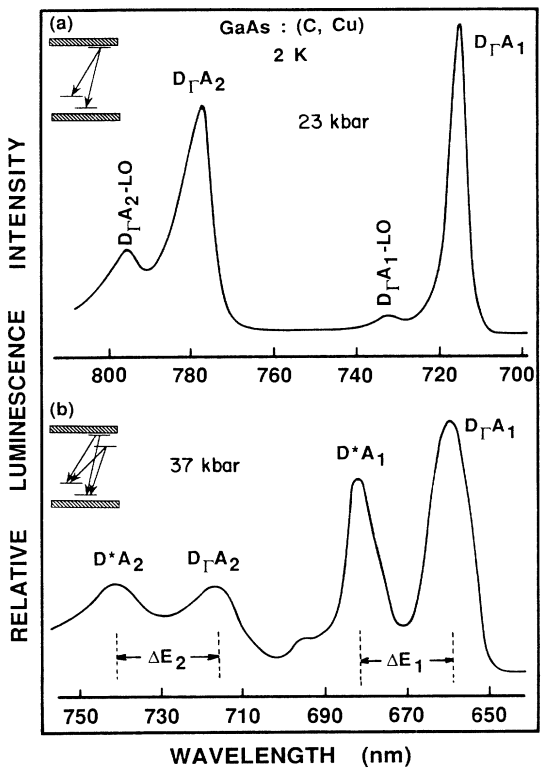

FIG. 4. Spectra of GaAs doped with two acceptors, shallow C and deep Cu acceptors, with binding energies at atmospheric pressure of 35 and 155 meV, respectively. Below the critical pressure of splitting [as shown in spectrum (a) at 23 kbar], two donor-acceptor peaks are observed, associated with the shallow and the deep acceptors. When the shallow DA peak exhibits a splitting, the deep one also does so [as shown in spectrum (b) at 37 kbar]. The splitting of each peak ($\Delta E_{1 \text{ or } 2}$ in the figure) stays identical for the shallow and deep DA peaks [spectrum (b)]. This tells clearly that the splitting of the DA peak is due to the splitting of the donor, as illustrated in the insets in the figure.

to higher energies.[37] It is interesting that at the pressure when the $D_\Gamma A_1$ peak exhibits the splitting, the lower-energy $D_\Gamma A_2$ peak also does so. $D^* A_1$ and $D^* A_2$ are observed in the same spectrum. Moreover, the splitting for the shallow acceptor DA peak $\Delta E_1 = E_{D_\Gamma A_1} - E_{D^* A_1}$ and that for the deep acceptor DA peak $\Delta E_2 = E_{D_\Gamma A_2} - E_{D^* A_2}$ stay the same [see 37 kbar in Fig. 4(b)]. These results indicate clearly that the splitting of the DA peaks is due to a splitting of the donor, as illustrated schematically in the insets of Fig. 4.

D. Detailed investigation around the splitting region

Several features confirm that the new peaks observed are recombinations of donor-acceptor type.

(i) They show an asymmetric broadening, together with a blueshift of the peak position when the excitation density is increased. As one knows, the asymmetry and blueshift of the $D_\Gamma A$ in GaAs are very small, since (a) GaAs is a direct gap material and it is very difficult to saturate the distant $D_\Gamma A$ pair luminescence, and (b) the GaAs crystals are usually quite pure, and high purity means a larger average separation for the DA pairs and a consequent smaller variation in the Coulomb term.[38] While complete sets of discrete close DA pair luminescence have been so successfully observed in indirect gap material, it has not been possible to observe the discrete close $D_\Gamma A$ pair luminescence in GaAs. In our experiment, although we did not successfully observe the discrete close $D^* A$ or $D_X A$ pair luminescence either, the asymmetry and blueshift of $D^* A$ or $D_X A$ pair luminescence, however, are larger than those of $D_\Gamma A$. The blueshift observed for $D^* A$ for an excitation density increase of two orders of magnitude is about 5 meV, which is typical for the unsaturated portion of the DA recombination.[39]

(ii) Another well-known characteristic of DA recombination is the redshift of its peak position with time delay. The close-spaced pairs which have higher emission energies have a higher transition probability and, therefore, they decay first. The more-distant pairs which have lower emission energies will consequently dominate the spectrum for a longer time and cause the peak to shift to lower energies with time. An observable redshift of the new peaks, however, is only a few meV, which is rather small. This is explained below by similar reasons as above. The $D^* A$ and $D_X A$ observed immediately after laser pulse may result already from very distant-spaced pair recombination. With the delay of time, they are almost close to the low-energy cutoff corresponding to infinitely spaced DA recombination ($h\nu_\infty = E_g - E_A - E_{D^*}$), and will not show significant redshift. A typical time decay of $D^* A$ is displayed in the inset in Fig. 8. The decay process is close to a single exponential, since we measured the time dependence of a peak height at a particular energy and hence DA pairs with a particular separation. The decay time measured is 0.9 μs. A DA pair recombination with such a microsecond time decay will indeed be very difficult to saturate, and one always observes the distant DA pair recombination. This is actually similar to the case of DA recombination in GaAs at atmospheric pressure, where a small redshift is also observed.[38]

(iii) A most interesting phenomenon is that of selective excitation luminescence at pressures near the splitting region. This phenomenon provides evidence that the new peaks are due to donor-acceptor recombination, and is described below.

Around the pressure region where $D_\Gamma A$ exhibits the splitting, the peak which traces the shifting excitation laser energy is observed. As shown in Fig. 5 for a pressure of 33 kbar, spectrum (a) is measured with an excitation wavelength of 5145 Å from an Ar^+ laser. At this pressure, $D^* A$ is the lowest-energy luminescence, while $D_X A$ has not appeared yet. When the excitation photon energy is tuned below the band gap, however, a shifting peak M is observed on the high-energy side of $D^* A$. If the laser energy is changed, the peak energy is always about 28 meV below the laser energy [as shown in Figs. 5(b)–5(d)]. It merges into $D^* A$ on the low-energy side when the laser energy is low, and into $D_\Gamma A$ on the high-energy side when the laser energy is tuned above the band

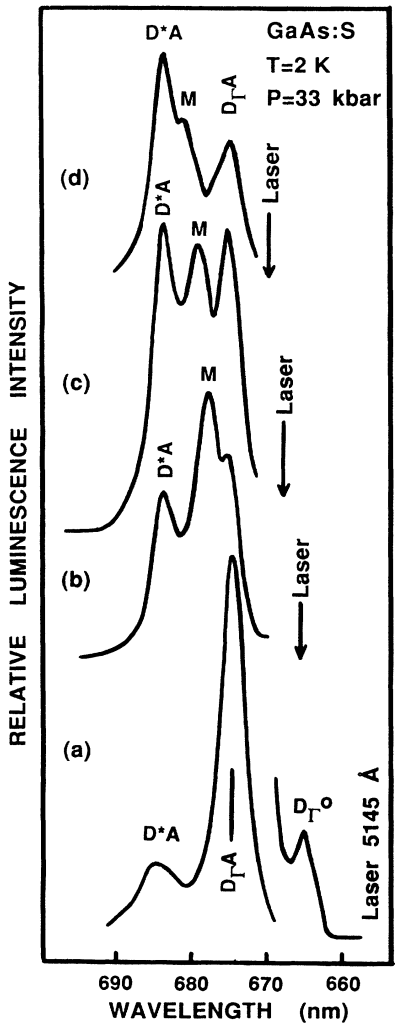

FIG. 5. Above-band-gap, 5145-Å excitation (a) and below-band-gap, selective excitation (b), (c), and (d) PL spectra for a GaAs:S sample at a hydrostatic pressure of 33 kbar. Arrows in the figure indicate the excitation wavelength of the laser. The peak positions of $D_\Gamma A$ and $D^* A$ do not change significantly with laser energy, while on the high-energy side of $D^* A$ a peak M, which shifts with the exciting laser energy, is observed when the laser energy is tuned below the band gap. M merges into $D^* A$ on the low-energy side when the excitation laser energy is low, and merges into $D_\Gamma A$ on the high-energy side, and cannot be observed when the excitation laser energy is higher than the band gap. The nature of peak M is discussed in the text.

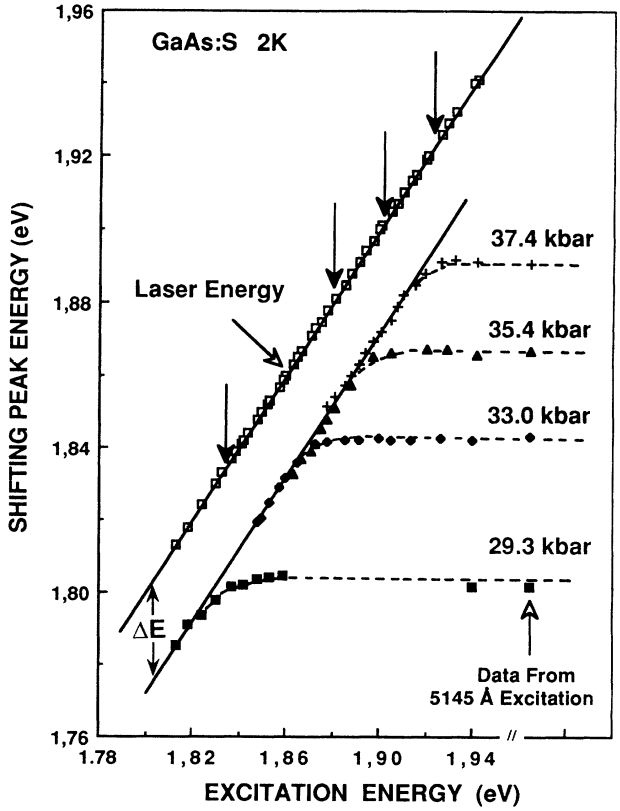

FIG. 6. The energy position of the shifting peak (M) plotted vs the excitation laser energy observed at different pressures around the splitting region. The arrows in the figure indicate energies of the band gaps corresponding to each pressure. It can be seen that the shifting peak is observed as long as the laser energy is below the band gap. If the excitation laser energy is changed, the energy separation ΔE between the laser energy and that of peak M remains constant (about 28 meV). For above-band-gap excitation, M merges into $D_\Gamma A$. No significant difference of ΔE is observed at the different pressures investigated. The lines drawn in the figure are simply to guide the eyes.

gap. We did not observe a shifting peak on the high-energy side of $D_\Gamma A$, although similar weak phenomena were reported at atmospheric pressure also for the $D_\Gamma A$ peak.[40] The shifting peak M is observed at different pressures, and in Fig. 6 we plot the energy position of the peak as a function of the laser photon energy. The arrows in the figure indicate the energies of the band gap corresponding to each pressure. It is clear from the figure that the shifting peak appears as long as the excitation energy is below the band gap, and it is always about $\Delta E = 28$ meV below the laser energy for all pressures.

The shifting peak M is too broad to be the Raman line of the laser which was sometimes observed. It is our conclusion that M is due to the resonant excitation of an electron on the donor while creating an excited hole on an adjacent acceptor. The excited hole would afterwards relax quickly to its ground state and then recombine with the electron on the donor, as illustrated in the inset in Fig. 7. The shifting M must be related to $D^* A$ instead of $D_\Gamma A$, since if M is related to $D_\Gamma A$, the shifting peak should have a low-energy cutoff at energy corresponding to the limiting photon energy of infinitely distant $D_\Gamma A$ pairs. However, what we observe is that M extends all the way down to the $D^* A$ peak.

Changing the laser energy changes the excitation of pairs with different separations. For sufficiently separated pairs, the photon energy required to create a pair (with a pair separation R) with an excited hole is

$$h\nu_{EX} = E_g - E'_A - E_{D^*} + e^2/\epsilon R \ , \qquad (1)$$

where E'_A is the energy of the excited state of the hole

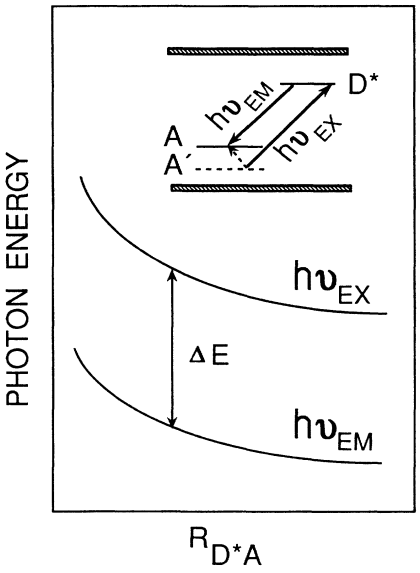

FIG. 7. Energy diagram drawn schematically in order to understand the shifting peak M. The excitation ($h\nu_{EX}$) creates an electron on the donor and an excited hole on the acceptor. The hole relaxes quickly to its ground state and then recombines with the electron on the donor, resulting in emission ($h\nu_{EM}$) as illustrated in the inset. By changing the excitation photon energy, the excitation of pairs with different separations (R_{D^*A}) is selected. However, the energy separation (ΔE) of the excitation photon and the emission peak stay constant, which is proposed to be the energy separation between the excited state and ground state of the acceptor.

with respect to the valence band, and E_{D^*} is the energy of the D^* donor state relative to the conduction-band edge. The other symbols have their usual meanings. The emission energy of the recombination of the pair with the hole on the ground state is

$$h\nu_{EM}=E_g-E_A-E_{D^*}+e^2/\epsilon R \ , \tag{2}$$

where E_A is the energy of the ground state of the hole with respect to the valence band. The difference between the excitation and emission energy will then be

$$\Delta E=h\nu_{EX}-h\nu_{EM}=E_A-E'_A \ , \tag{3}$$

which is the difference between the energy of the ground state and the excited state of the hole on the acceptor, independent of the pair separation R (see Fig. 7). We therefore judge from Fig. 6 that for the excited state of the acceptor, ΔE is about 28 meV. This value does not change significantly as the pressure increases from about 29 to 37 kbar. The value falls between the energy separations from the excited $2P_{3/2}$ to the ground $1S_{3/2}$ state of the shallow acceptors in GaAs (Ref. 40) and GaP.[41,42] The fact that ΔE is larger than the energy separation between $2P_{3/2}$ and $1S_{3/2}$ in GaAs may be accounted for by the involvement of higher excited states of the acceptor in the experiment on the selective excitation luminescence.

If our identification of peak M is true, one will expect that the peak M should decay faster than the D^*A peak, since M is related to the closer D^*A pair transition. This is demonstrated by the time-resolved spectra in Fig. 8. The spectra in Fig. 8 were measured at the same pressure as those in Fig. 5, i.e., with the excitation laser energy lying just below the band gap, and with the shifting peak M having just appeared. It can be seen that *during* the laser pulse, the peak M dominates the spectrum [Fig. 8(a)]. However, it has a shorter decay time, and decreases in intensity more quickly than D^*A with the delay of time. At about 300 ns after the end of the laser pulse, the spectrum is dominated by the D^*A peak [Fig. 8(c)]. The shorter decay of the peak M confirms our conclusion above that it is related to the closer pair transitions. If one takes a careful look at the spectra in Fig. 8, one will discover that although the D^*A peak shows very little

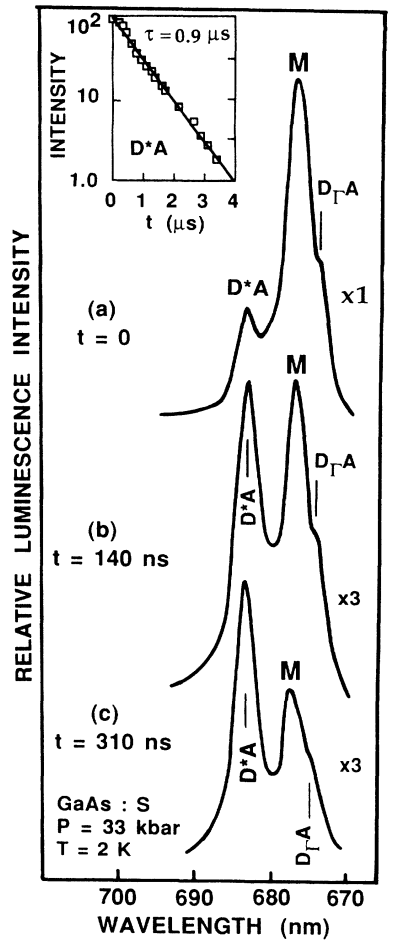

FIG. 8. Time-resolved PL spectra for a sulfur-doped GaAs sample, measured at the same pressure as that in Fig. 5 with the excitation laser energy lying just below the band gap. The shifting peak M just appears in this case. It dominates the spectrum during the laser pulse (a). With the delay of time, however, the peak M, since it is related to closer pair recombination, decreases in intensity faster than the D^*A peak [spectra (b) and (c)]. A more obvious redshift of the peak M in comparison with D^*A in the time scale studied and an asymmetrical line shape of the peak M observed with the delay of time are explained in the text. The inset in the figure illustrates a typical time decay of the D^*A peak at a particular pair-recombination energy. It is found to have a characteristic decay time of 0.9 μs.

redshift in the time scale shown, the peak M manifests a larger redshift than D^*A and a quicker decrease in intensity on the high-energy side. This is exactly as one would expect if the peak M consists of several DA recombinations of different separations with their $h\nu_{EX}$ in Eq. (1) having the same energy as the excitation laser energy due to their different excited states involved. That is, for instance,

$$h\nu_{EX1}=E_g-E'_{A1}-E_{D^*}+e^2/\epsilon R \ ,$$

$$h\nu_{EX2}=E_g-E'_{A2}-E_{D^*}+e^2/\epsilon R_2 \ ,$$

and

$$h\nu_{EX1}=h\nu_{EX2} \ .$$

However, their emissions (not resolvable in the peak M) have different energies,

$$h\nu_{EM1}=E_g-E_A-E_{D^*}+e^2/\epsilon R_1 \ ,$$

$$h\nu_{EM2}=E_g-E_A-E_{D^*}+e^2/\epsilon R_2 \ ,$$

and

$$h\nu_{EM1}\neq h\nu_{EM2} \ .$$

An emission related to a pair of smaller separation (on the high-energy side of M) will decay faster than one related to a pair of larger separation (on the low-energy side of M).

IV. DISCUSSION

The $D_\Gamma A$ peak, originating from an acceptor and a donor associated with the Γ-band minimum, crosses two other DA peaks when the hydrostatic pressure exceeds critical values. It has been well established in Sec. III that the new peaks are donor-acceptor-like and originate from the splitting of the donor. One of the peaks, $D_X A$, tracks the X-band minimum (-1.3 meV/kbar) when the pressure is changed and is judged to be involved with a donor associated with the X conduction-band edge. The other peak, D^*A, however, has a pressure coefficient of about 1 meV/kbar. It seems that the donor state involved does not track any of the known conduction-band minima. It is, however, in many ways similar to the DX centers observed in GaAs and related alloys.

(i) *The omnipresence of D^*A.* Like the DX centers, D^* has been observed in different samples of donor dopant on a group-III site (for example, Si) or a group-V site (for example, S), as well as in bulk material. It gives rise to a donor-acceptor-like recombination when the applied hydrostatic pressure exceeds a critical value. When the energy level of D^* is below that of D_Γ, the luminescence intensity of D^*A is similar to that of $D_\Gamma A$ before splitting. In general, a sample with strong $D_\Gamma A$ luminescence will also have a strong D^*A luminescence in our investigation. It is hard to tell quantitatively the concentration of a defect from its luminescence intensity, since the luminescence intensity depends not only on the numbers of centers, but also on the efficiency of their excitation and their radiative versus nonradiative recombination. However, since the energy structure and the relative PL intensities of the donor states (D_Γ, D^*, and D_X) are insensitive to the doping of the sample but are directly related to the pressure-induced energy band structure, it is tempting to assume that D_Γ, D^*, and D_X are different states of the same donor. This is very similar to the DX center, which has a concentration of the deep state almost equal to the number of shallow donors in various samples, and the present understanding of the DX problem is that the shallow and deep states are different configurations of the same donor. It seems very unlikely that D^* is another donorlike state existing in different types of GaAs samples but having nothing to do with the DX center.

(ii) *The critical pressure.* The value of the pressure at which the D^*A recombination in PL is observed is about 28 kbar. At this pressure, the band structure of GaAs is very similar to that of $Al_xGa_{1-x}As$ for the composition x at which the DX center starts to be observable in space charge measurement. This critical pressure is also very close to that for the observation of the DX center in GaAs in the DLTS measurement when the peak is fully developed.[13]

(iii) *The energy position at atmospheric pressure.* When D^*A first appears in the PL, the energy of the peak is about 1.810 eV. Using the pressure coefficient of 1 meV/kbar and extrapolating the D^*A energy to atmospheric pressure, we get a position about 260 meV above the Γ conduction-band minimum. Correcting for the acceptor binding energy and the Coulomb energy, we estimate the donor level to be 270 meV above the Γ minimum at atmospheric pressure. This value is in very good agreement with recent results from DLTS measurements on the DX level in degenerately n-doped GaAs.[43]

(iv) *The pressure coefficient.* The pressure dependence of the D^* energy level is 1 meV/kbar, which does not track any band edge. This newly observed pressure coefficient agrees neither with L-band-like composition dependence in AlGaAs alloy measurements[44] nor with the average dependences[23] of band minima (Γ, X, L). It is also in contrast to the results of pressure measurements on the DX center in $Al_xGa_{1-x}As$ alloys, where the pressure coefficient of the ionization energy of the deep donor was dominated by the L minimum.[31,32] In fact, as far as we know, in GaAs no pressure coefficient of the pressure-induced deep center (or the DX center) observed agrees with that of the DX center observed in $Al_xGa_{1-x}As$ alloys.[13,45] Instead, the pressure coefficient of 1 meV/kbar we observed is actually close to the average dependences of band minima (Γ, X, L) multiplied by the density of states for each of these band edges.

(v) *The comparison with PL in alloys.* The results of PL in $Al_xGa_{1-x}As$ alloys obtained by Henning *et al.*[18] revealed that, at an Al composition of $x>x_0=0.22$, a DA peak resembling the D^*A is observed here. This DA peak was proposed to be the luminescence related to the DX center. Its energy position and the shape of the spectra are very similar to the D^*A peak in our pressure experiment on GaAs. Since at an Al composition of x_0 the structure of the conduction band in the alloy is very similar to that of GaAs under the critical hydrostatic pressure here, it is not unlikely that Henning *et al.* were ob-

serving the corresponding D^*A luminescence in alloys.

We believe that the omnipresent D^* state is important, especially for the understanding of the DX center. If D^* is the DX center as observed in photoluminescence, however, then we are observing a DX center which does not show a large lattice relaxation in the emission process. The phonon replica on the lower-energy side of D^*A has an energy separation from the zero-phonon peak of about 36 meV. This agrees with the longitudinal optical phonon in the Brillouin-zone center of GaAs, LO^{Γ}. Its Huang-Rhys factor S is observed to be as small as $S=0.3\pm0.1$ Furthermore, the most puzzling feature of our investigation is that, in spite of all the similarities in the behavior of the D^* and the DX center, no photoquenching could be observed for our D^*A peak on the measured time scale (from several seconds to tens of minutes). One of the fingerprints of the DX center in alloys first reported by Lang *et al.*[1,2] is its PPC effect at low temperature. The corresponding photoquenching of the luminescence of a DX center could be expected in low-temperature PL measurements. That is, the luminescence intensity would be quenched if we photoionized the DX center as in a PPC experiment, since the center would not be able to recapture an electron unless the sample temperature is sufficiently high. In our PL measurement, the energy of the incident excitation photon is always above the threshold energy for the photoionization of the DX center. We would then expect a quenching of the luminescence of a DX center if it is monitored on the right time scale.

Although our new peaks have very similar properties to those of the proposed DX centers observed by Henning *et al.*[18] in alloys (they do not seem to have observed the photoquenching effect of the luminescence for their DX center, either), the absence of the photoquenching effect makes it difficult for us to prove that our D^* is the DX center. Henning *et al.*[18] proposed a DX-center model without resorting to an extreme lattice distortion as the explanation of their small S factor, DX-center luminescence. From their proposed DX-center model, one would still expect a DX center with a PPC and a photoquenching effect. However, we cannot exclude the possibility that the DX center would not show any photoquenching of the luminescence. The purely athermal or hot-electron-capture process at low temperature proposed by Theis *et al.*[46] is a good example which may account partly for our nonphotoquenching DX luminescence. Since we always use an incident photon energy of above 1.8 eV in order to observe the D^*A peak, we are probably continuously generating hot electrons. These hot electrons may be captured by the DX center at low temperature. It would be sufficient if the optical pumping employed keeps a fraction of the donor in the deep-state configuration, which would then prevent us from observing the photoquenching effect. It is also possible that in photoluminescence, there exists another unknown feeding level for the DX center.

In spite of the fact that the results of magnetic-susceptibility measurements indicate that the DX center is a paramagnetic donor with an unpaired electron,[47] the negative-U model of the DX center proposed recently[23] has been quite successful in explaining many properties of the DX center. Although we proposed that the D^* is related to the DX center, all the above experimental results and discussions suggest a positive-U model of the D^* electron trap. A negative-U model of the donor would, however, predict for PL measurements no asymmetry and blue shift at high excitation density, no red shift with time delay, and no shifting peak M, since there would be no Coulomb effect in the DA recombination. Could the deep donor related to the DX center have two configurations? One shows the small lattice relaxation and nonphotoquenching as the D^* state observed here, while the other shows large lattice relaxation and photoquenching which determines the electrical characteristics of the material.[48,49] If this is true, it would be consistent with the idea of a negative U center if the small lattice relaxation state could be the unrelaxed neutral donor state.[50] Nevertheless, further investigations are required in order to answer the question, and there is still a long way to go before the complicated DX center is fully understood.

We would like to make two final comments before proceeding to the last section. Firstly, it seems quite surprising that no report of D^*A and D_XA existing in GaAs was ever published by other research groups, even though pressure is nowadays commonly used for investigating the effects of band structure on semiconductor properties. This may be due to the selection of samples. As described in Sec. III C the observation of D^*A and D_XA luminescence is much more difficult if an unsuitably doped GaAs sample is chosen. Secondly, the radiative recombination of isolated nitrogen-bound excitons N_X is very frequently observed in our luminescence measurements of GaAs under hydrostatic pressure. It not only appears in the luminescence spectra of GaAs for pressures above 22 kbar, but also has a pressure dependence incidentally very close to that of the L-band edge. However, the nature of the N_X luminescence as being due to the isolated nitrogen-bound exciton has been well established, and should not in any case be mistaken as being due to a donor state like D^* (or the DX center).[51]

V. SUMMARY

Spectroscopic investigations of GaAs under hydrostatic pressure reveal that near-band-gap donor-acceptor recombination $D_{\Gamma}A$ crosses two other DA-recombination peaks at pressures higher than 28 kbar. This is observed in many GaAs crystals containing different donor dopants. That the new peaks are due to transitions of the donor-acceptor type has been well established by excitation power dependence, time-decay measurement, and selective excitation luminescence investigations. A sample doped with different acceptors (one shallow and one deep) shows that when the shallow DA transition exhibits the splitting, the deep one shows the same phenomenon. This indicates clearly that the origin of the splitting of the DA peak is the splitting of the donor involved in the recombination. We have observed three donor states in GaAs as the band structure is changed by pressure: D_{Γ}, D^*, and D_X. Their pressure dependence shows that D_{Γ} and D_X track the Γ- and X-

band edges, respectively, and are believed to be donor states associated with each of these conduction-band minima. D^* does not follow any particular conduction-band edge. It is, however, in many respects similar to the much-discussed DX center studied in space-charge measurements in $Al_xGa_{1-x}As$ alloys or in GaAs under hydrostatic pressure, although it exhibits a small Huang-Rhys factor, i.e., a small lattice relaxation in emission, and does not show photoquenching within the time scale of our measurements.

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