

## Pressure dependence of the $DX$ center in $Ga_{1-x}Al_xAs:Te$

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The pressure dependence of the  $DX$  center in Te-doped ternary alloy  $Ga_{1-x}Al_xAs$  with  $x=0.15$ , 0.25, and 0.35 has been studied. The pressure coefficients of the activation energies for emission and capture as well as the pressure coefficient of the thermal ionization energy were found to change sign when the band gap of  $Ga_{1-x}Al_xAs$  changed from direct to indirect. The compositional dependence of these energies at atmospheric pressure has also been extrapolated from the pressure dependence. Similarities between the effects of changing pressure and Al mole fraction suggested that the properties of the  $DX$  center depend mainly on the host semiconductor conduction-band structure. The difference in the pressure dependence of the  $DX$  center when the band gap is direct as opposed to indirect suggests that the defect wave function has considerable contribution from the conduction-band minima near the  $X$  point of the Brillouin zone and not just from the  $L$ -point minima as has been proposed by many authors.

### I. INTRODUCTION

The properties of deep donors known as the  $DX$  centers in the  $Ga_{1-x}Al_xAs$  alloy system have been studied for over a decade since their discovery by Lang and co-workers.<sup>1,2</sup> These centers have attracted much attention because they have been found to influence the performance of high-speed devices such as modulation-doped field-effect transistors (also known as high-electron-mobility transistors). It has been found that  $DX$  centers are present in all  $n$ -type  $Ga_{1-x}Al_xAs$  with  $x \geq 0.25$ . The number of centers in a sample is always of the order of the donor atoms independent of the kind of donor atoms (Si, Sn, S, Se, or Te) and of the method of growth.<sup>1-6</sup> Some of the unusual properties of the  $DX$  centers are that both the emission and capture processes of electrons are thermally activated;<sup>2,3,6</sup> samples containing  $DX$  centers show persistent photoconductivity<sup>7</sup> (PPC) at low temperature and there is a large Stokes shift between the optical and thermal ionization energies. To explain the unusual properties of the  $DX$  center, Lang *et al.*<sup>1,2</sup> proposed that the  $DX$  center is a complex formed by a donor atom and an intrinsic defect such as an As vacancy. Using a configuration-coordinate diagram model with a large lattice relaxation, Lang and co-workers<sup>8</sup> were able to explain the activated emission and capture processes and PPC in the  $DX$  centers. Besides the pioneering work of

Lang and co-workers, the properties of the  $DX$  centers have been extensively studied as a function of the Al mole fraction  $x$ . For example, using the Hall measurement, Springthorpe *et al.*<sup>3</sup> and Chand *et al.*<sup>5</sup> have studied systematically the dependence of the thermal ionization energy on  $x$  and found that the  $DX$  center seemed to follow closely the conduction-band minima at the  $L$  point of the Brillouin zone. These and other results<sup>9,10</sup> have led to the suggestion that the  $DX$  center wave function is derived mainly from the  $L$  conduction-band minima. In the course of these studies it was found that pressure could modify the properties of the  $DX$  centers in a way similar to changing the Al concentration.<sup>11,12</sup> This was generally explained by the fact that pressure can lower the conduction-band valleys at the  $X$  point relative to the  $\Gamma$  and  $L$  valleys in the same way as alloying. Recently Mizuta *et al.*<sup>13,14</sup> found that deep donors with emission properties similar to the  $DX$  center can be induced in GaAs:Si with pressures larger than about 24 kbar. This result was reproduced by Li and co-workers<sup>15,16</sup> who further showed that these pressure-induced deep centers have a very large optical ionization energy as in the  $DX$  centers. These new results suggest that vacancies are not necessary for  $DX$  center formation and have led to many new models of the  $DX$  center involving no vacancies and to proposals that the  $DX$  center has small lattice relaxation.<sup>17-19</sup> More recently, it has been suggested that the

$DX$  center is a “negative- $U$  center” so that a  $DX$  center in its ground state has two electron rather than one.<sup>20,21</sup>

So far most studies of the pressure dependence of the  $DX$  centers has been limited to a narrow range of pressure.<sup>11–13,15</sup> It is well known that pressure decreases the energy of the  $X$  conduction-band minima in GaAs and  $Ga_{1-x}Al_xAs$  alloys so that at high enough pressure the band gap of the semiconductor will change from direct to indirect. Thus pressure can provide important insights as to how the properties of the  $DX$  center depend on the band structure by changing the conduction-band structure. Although this band-structure modification can also be achieved by alloying with Al which lowers the  $X$  valleys relative to the  $\Gamma$  valley, there is a difference between the two methods in that alloying *increases* the energy of the  $X$  minima while pressure *decreases* their energy. In addition, varying pressure has the advantage that variations in  $DX$  center properties due to different sample thermal histories and alloy fluctuations can be avoided.

In this paper we present the results of an investigation into both the effect of pressure and alloy composition on the emission and capture properties of the  $DX$  center in Te-doped  $Ga_{1-x}Al_xAs$  samples.<sup>22</sup> The pressure coefficients of the activation energies for both emission and capture are found to change sign when the band gap switches from direct to indirect. The  $DX$  center energy is found to track the  $L$  valleys only approximately as a function of pressure. Significant deviation between the pressure dependence of the  $L$  valleys and of the  $DX$  center occurs when the band gaps is indirect. Although the  $DX$  center is metastable and not observable at atmospheric pressure in the 15% and 25% Al samples, we are able to extrapolate, from the results obtained under pressure, the emission and capture activation energies of the metastable  $DX$  center at ambient pressure. We found that the emission activation energy is compositionally dependent in Te-doped  $Ga_{1-x}Al_xAs$  samples in contrast to what has been reported in Si-doped  $Ga_{1-x}Al_xAs$ .<sup>23</sup> Our results suggest that the  $DX$  center wave function is derived from the conduction band throughout the entire Brillouin zone rather than from the  $L$  valleys only. The contribution of the conduction-band minima at the  $X$  points is especially significant in understanding the behavior of the  $DX$  center when the band gap is indirect. Finally a quantitative comparison of our results with the predictions of the negative- $U$  model of Chadi and Chang<sup>20</sup> pointed to directions for refining the theoretical models.

## II. EXPERIMENTAL PROCEDURE

Our experiments were performed on Schottky barrier diodes fabricated from  $Ga_{1-x}Al_xAs$  epilayers doped with  $5 \times 10^{16} \text{ cm}^{-3}$  of Te and grown by liquid-phase epitaxy on  $n^+$ -type GaAs substrates. Samples with 15%, 25%, and 35% Al have been studied. The Al mole fraction was verified by Raman scattering. Schottky barriers were fabricated on large wafers about 100  $\mu\text{m}$  thick by evaporating Al onto the epilayer. Ohmic contacts to the substrate were formed by evaporation of the AuGe alloy followed by a 450  $^\circ\text{C}$  annealing for 1 min. Chips typically

$200 \times 20 \mu\text{m}^2$  in size were cut from the wafers and the cut sides of the chips were etched to reduce reverse bias leakage current. Quasihydrostatic pressure was applied to the sample by means of a gasketed diamond-anvil high-pressure cell (DAC). Copper wires were introduced into the cell to contact the sample using the method described by Erskine *et al.*<sup>24</sup> The sample inside the DAC was surrounded by epoxy and soft  $\text{CaSO}_4$  powder mixed with vacuum grease as the pressure medium. Pressure was determined by the standard ruby fluorescence technique using several ruby chips placed around the sample. The pressure inhomogeneity inside of the cell was estimated to be typically about  $\pm 1$  kbar by measuring the variation in the pressure of these ruby chips. Uniaxial stress may split the  $DX$  centers whose lattice relaxations are oriented along different directions relative to the stress axis. Since we did not observe splitting of the  $DX$  center, this suggested that any uniaxial stress which resulted from the pressure inhomogeneity inside the cell was too small to be observed. The cell was pressurized always at room temperature with a hydraulic press. The pressure was locked in place by a retainer ring and the cell removed from the press during measurements. We found that the cell pressure increased slightly on cooling from room temperature to liquid-nitrogen temperature. Most of this increase occurred between room temperature and 200 K. As our experiments were typically performed below 200 K, this pressure increase had a minimal effect on our results. However, it was necessary to calibrate the pressure at the temperature of the experiment.

Deep levels in samples were measured with conventional constant-voltage deep-level transient spectroscopy (DLTS) using a Boonton 72B capacitance meter and a PAR Model No. 162 dual-channel boxcar integrator. The sample temperature was monitored by a calibrated Si diode thermometer attached with vacuum grease to the diamond anvil closest to the sample. The cell temperature was changed very slowly (about 2 K/min) during DLTS runs to minimize the temperature difference between the sample and the diode sensor. The emission rates ( $e_n$ ) of the deep center were determined from the DLTS spectra. To measure the capture rates the standard majority-carriers pulse method<sup>8</sup> was used at the temperature corresponding to the DLTS peaks. The amplitudes of transient capacitance signals were recorded as a function of the width of the pulses used to fill the traps. The capture time constant ( $\tau_c$ ) was determined in a way analogous to the method of Lang.<sup>8</sup> As discussed by several authors, the capture process in  $Ga_{1-x}Al_xAs$  is highly nonexponential due to several factors.<sup>25,26</sup> One of reasons is the large number of  $DX$  centers relative to the number of free carriers so that the concentration of electrons in the conduction band is not constant during capture. Because of this we have determined  $\tau_c$  from the  $\frac{1}{3}$ -signal points rather than the  $\frac{1}{2}$ -signal points used by Lang.<sup>8</sup>

## III. EXPERIMENTAL RESULT

In all samples used in this work the emission rate ( $e_n$ ) and capture rate ( $\tau_c^{-1}$ ) were found to have an activated

temperature dependence of the form

$$e_n/T^2 = A_e \exp(-E_e/kT) \quad (1)$$

and

$$(\tau_c)^{-1} = A_c \exp(-E_c/kT), \quad (2)$$

where  $E_e$  and  $E_c$  denote, respectively, the activation energies for emission and capture of an electron. In Fig. 1 some Arrhenius plots of  $e_n/T^2$  versus  $T^{-1}$  in an  $x=0.25$  sample at different pressures are shown and the inset shows a typical DLTS spectrum in the same sample. It has been reported by several authors<sup>8,27,28</sup> that DLTS spectra of samples containing  $DX$  centers often show two or three peaks, typically a main peak identified with the  $DX$  center accompanied by one or two smaller peaks. We have made similar observations in our samples both at ambient pressure (35% sample) and under pressure. For example, in the 15% samples two small peaks appeared at the higher temperature side of the main peak. In the 25% samples two smaller peaks were sometimes observed with one on each side of the main peak. In the 35% samples a peak could be resolved at the lower temperature side of the main peak at low pressure. The origin of these additional peaks in the DLTS spectra is not understood at the present time. Some authors<sup>29</sup> have suggested that these represent  $DX$  centers with different local environments in the alloy. Others<sup>27</sup> have suggested that these peaks represent different configurations of the  $DX$  center. We have utilized the pressure dependence of the observed peaks to distinguish them from the  $DX$  center peaks. Typically the  $DX$  center peak strength shows a maximum at some pressure depending on the Al mole fraction, whereas the strength of the satellite peaks are not sensitive to pressure. In Fig. 2 we show how the strength of the  $DX$  center peak in the DLTS spectra varies with pressure in the 15% Al sample. We note the similarity between the pressure dependence of the  $DX$  center peak intensity and its Al concentration dependence.<sup>8</sup> Based on

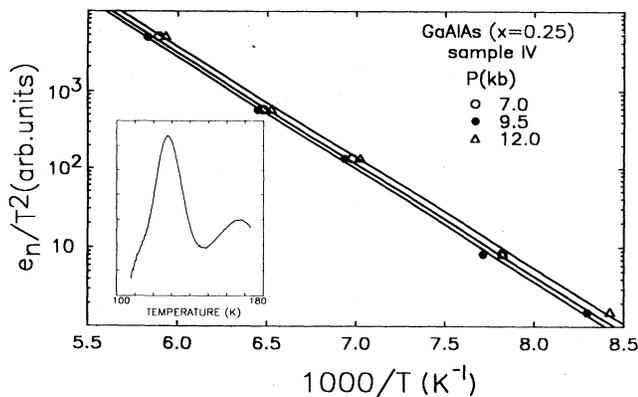


FIG. 1. Arrhenius plot of  $e_n/T^2$  vs  $1/T$  for the  $DX$  center in a  $Ga_{0.75}Al_{0.25}As:Te$  sample under three different pressures. The inset shows a typical DLTS spectra in the sample at  $P=27$  kbar. Window times:  $t_1=0.5$  s,  $t_2=1$  s. Filling pulse width: 400 ms.

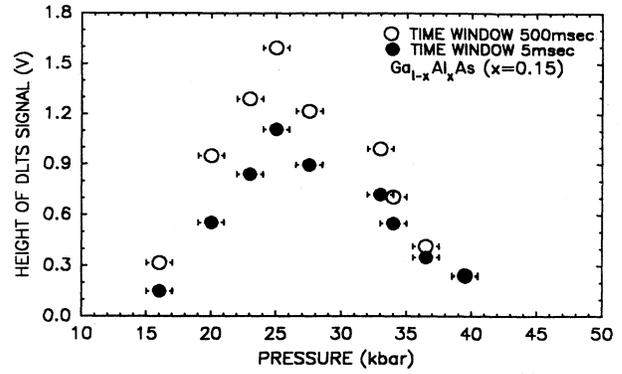


FIG. 2. Pressure dependence of the intensity of the main DLTS peak attributed to  $DX$  centers in a  $Ga_{0.85}Al_{0.15}As$  sample. The solid circles are for the 5-ms time window.

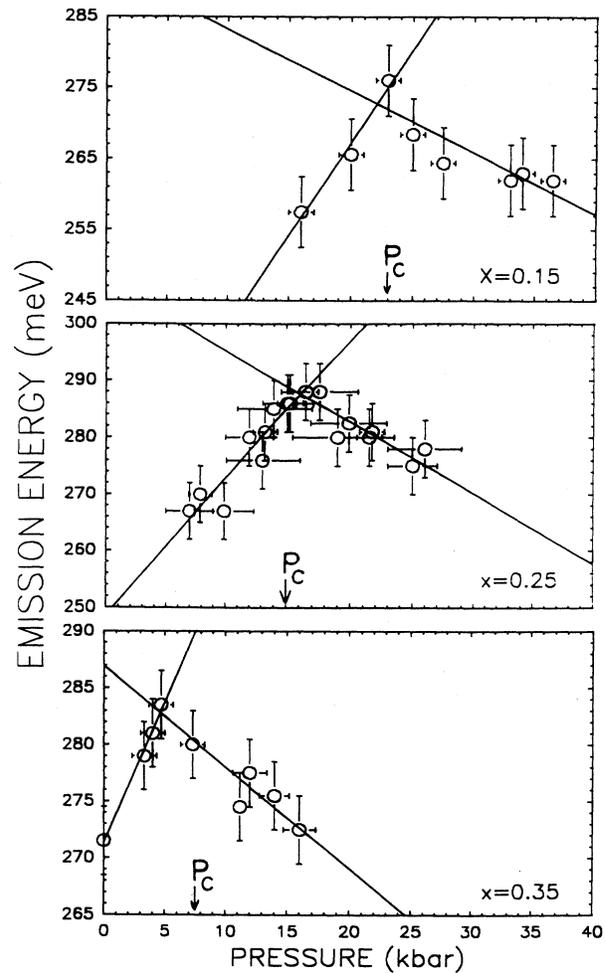


FIG. 3. Pressure-induced changes in the emission activation energy  $E_e$  in Te-doped  $Ga_{1-x}Al_xAs$ , with  $x=0.15$ , 0.25, and 0.35. The solid lines drawn through the experimental points represent the least-squares fit to the data. The arrows indicate the pressure ( $P_c$ ) where the band gap changes from direct to indirect.

these observations we can exclude the possibility that some of these satellite peaks were caused by splitting of the  $DX$  center induced by stress inhomogeneity.

We have observed slight variations in the DLTS spectra of the  $DX$  center and also in the capture rates from sample to sample. For instance, two 35% Al samples have been measured and the values of  $E_e = 0.27 \pm 0.01$  eV and  $E_c = 0.237 \pm 0.01$  eV are obtained in one sample at ambient pressure. The corresponding values were 0.28 and 0.239 eV in another sample. These values are to be compared with the values of  $0.33 \pm 0.03$  eV and  $0.26 \pm 0.03$  eV reported by Lang and Logan<sup>2,8</sup> in a Te-doped sample with  $x=0.36$ . In spite of the slight differences in the absolute values of  $E_e$  and  $E_c$  between individual samples their pressure dependences are quite similar. Figures 3 and 4 show the variations of  $E_e$  and  $E_c$  with pressure for all three alloy samples. The straight lines, which represent the least-squares fits drawn through the experimental points in these figures, show clearly the similarity in the pressure dependences of  $E_e$  and  $E_c$  in all three alloys. The pressure coefficients deduced from these fits are summarized in Table I for all three  $Ga_{1-x}Al_xAs$ :Te samples. In all three alloys we note that the pressure coefficients of both  $E_e$  and  $E_c$  abruptly change signs at some pressures ( $P_c$ ) which are very close to the pressures where the band gap of  $Ga_{1-x}Al_xAs$  is predicted to switch from direct to indirect (indicated by arrows in Figs. 3 and 4). The pressures where the  $X$  and  $\Gamma$  valleys are expected to cross have been calculated from the band-edge pressure coefficients ( $dE_\Gamma/dP = 12$  meV/kbar,  $dE_L/dP = 5.5$  meV/kbar, and  $dE_X/dP = -1.5$  meV/kbar) in conjunction with the alloy dependence of the band edges ( $E_\Gamma = 1.424 + 1.247x$  eV;  $E_L = 1.708 + 0.642x$  eV;  $E_X = 1.9 + 0.125x + 0.143x^2$  eV) given in Ref. 12. An interesting result we found is that the sum of the value of  $P_c$  (in kbar) and the percentage of the Al mole fraction in the  $Ga_{1-x}Al_xAs$  alloy is approximately constant:  $P_c + 100x \sim 40$ . This result suggested that *the effect of 1 kbar of pressure on the  $DX$  center is approximately equivalent to increasing the Al concentration by 1%*. This result can be justified presumably by the fact that pressure decreases the energy separation between the  $\Gamma$  and  $X$  conduction-band minima at the rate of 13 meV/kbar, while increasing the Al concentration decreases the same energy separation at the rate of 11.1

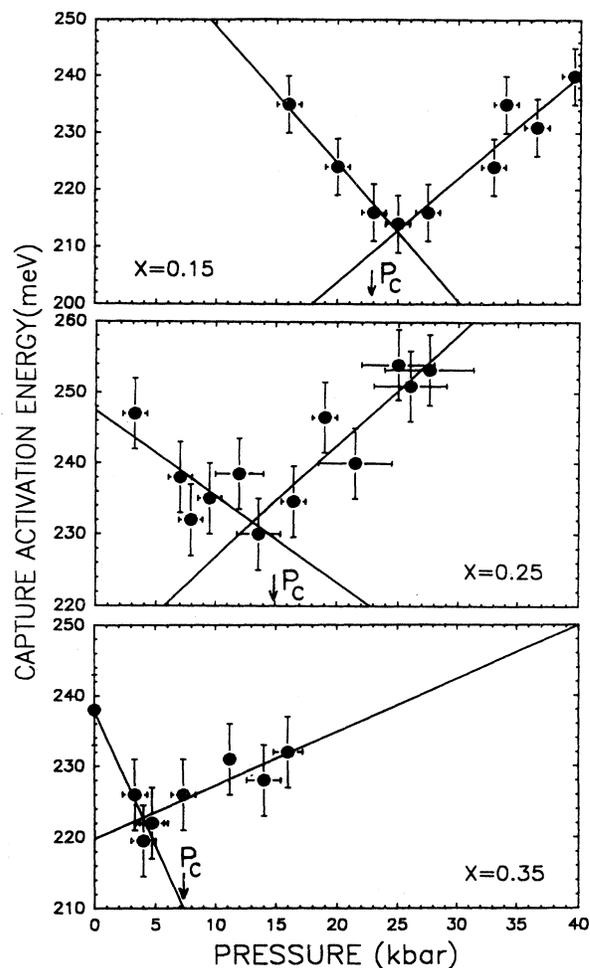


FIG. 4. Pressure-induced changes in the capture activation energy  $E_c$  in Te-doped  $Ga_{1-x}Al_xAs$  with three different Al concentrations. The solid lines drawn through the experimental points represent the least-squares fits to the data.

meV/(percent of Al). Finally, we note that the pressures at which the strength of the  $DX$  center reaches the maximum value coincide with  $P_c$  as can be seen by comparing Figs. 2 and 3.

TABLE I. Activation energies (extrapolated to 1 bar in meV) of the  $DX$  center and the pressure coefficients (in meV/kbar) in three alloys of  $Ga_{1-x}Al_xAs$ :Te with Al mole fraction of 0.15, 0.25, and 0.35.

	$x=0.15$		$x=0.25$		$x=0.35$	
	Direct gap	Indirect gap	Direct gap	Indirect gap	Direct gap	Indirect gap
$dE_e/dP$	2.54	-0.9	2.41	-1.25	2.46	-0.9
$dE_c/dP$	-2.5	1.8	-1.3	1.6	-3.8	0.75
$dE_T/dP$	4.9	-2.7	4.7	-2.8	4.5	-1.7
$E_e(P=1 \text{ bar})$	216 $\pm$ 5		244 $\pm$ 5		272 $\pm$ 5	
$E_c(P=1 \text{ bar})$	272 $\pm$ 5		249 $\pm$ 5		238 $\pm$ 5	
$E_T(P=1 \text{ bar})$	-56 $\pm$ 5		-5 $\pm$ 5		34 $\pm$ 5	

## IV. ANALYSIS OF RESULTS AND DISCUSSION

So far there have been several studies on the effect of alloy composition on the properties of the  $DX$  center. In these ambient-pressure studies the Al concentration is typically larger than 25% since at lower Al mole fraction the  $DX$  centers become metastable and are not observed. Using pressure we can lower the  $DX$  center energy in the low-Al concentration samples to below the conduction band so that they become observable. By extrapolation we can deduce the properties of the metastable  $DX$  at ambient pressure. Using the pressure-dependent results in Figs. 3 and 4 we have extrapolated the values of  $E_e$  and  $E_c$  for the  $DX$  center in samples with  $x=0.15$  and  $0.25$  at ambient pressure. These results are listed in Table I and shown in Fig. 5 together with the experimental points for  $x=0.35$ . In Fig. 5 the straight lines represent least-squares fits to the experimental points with the expressions

$$E_e = 175 + 275x \text{ meV} \quad (3)$$

and

$$E_c = 296 - 172.5x \text{ meV} \quad (4)$$

For comparison, we note that Mooney *et al.*<sup>23</sup> and Calleja *et al.*<sup>9</sup> have studied the dependence of  $E_e$  and  $E_c$  on Al concentration in  $\text{Ga}_{1-x}\text{Al}_x\text{As}$  doped with Si for  $x$  both below and above the critical value  $x_c \approx 0.4$  where

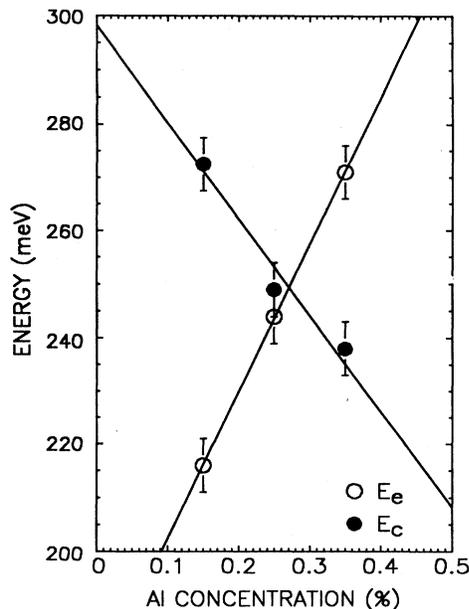


FIG. 5. Variations of activation energies for emission ( $E_e$ ) and capture ( $E_c$ ) of the  $DX$  center in  $\text{Ga}_{1-x}\text{Al}_x\text{As:Te}$  vs alloy composition in the direct-band-gap region at ambient pressure. The data points for  $x=0.15$  and  $0.25$  have been obtained by extrapolating the pressure-dependent values of  $E_e$  and  $E_c$  to 1 bar. The solid lines drawn through the circles represent the least-squares fits to the data.

the band gap changes from direct to indirect. These authors found that, with an increase in  $x$ ,  $E_c$  decreases when the band gap is direct and then increases when the band gap becomes indirect. Thus their results on  $E_c$  are in qualitative agreement with Eq. (4) and with the pressure dependence of  $E_c$  shown in Fig. 4. However, Mooney *et al.*<sup>23</sup> found no variation, beyond experimental uncertainty, in  $E_e$  with  $x$  in contrast to our results as represented by Eq. (3) and Fig. 3. One should note that the maximum change in  $E_e$  from Eq. (3) was less than 90 meV when  $x$  varies from 0.2 to 0.5. The changes in  $E_e$  with pressure shown in Fig. 4 are even smaller. Compared with the experimental uncertainties in Refs. 9 and 23 caused by sample variations, these changes are probably too small to be observed in those studies. In addition there may be a possible difference in behavior between the dopants used in those experiments and in ours (Si versus Te). Thus our results are not inconsistent with those of Mooney *et al.*<sup>23</sup> The alloy dependence of  $E_e$  as represented by Eq. (3) is quite consistent with the pressure dependence of  $E_e$ . From Table I we see that in all three samples the pressure coefficient  $dE_e/dP$  is about 2.5 meV/kbar. On the other hand the change in  $E_e$  with Al concentration is 2.75 meV/(percent of Al) from Eq. (3).

Based on the finding that  $E_e$  is constant and independent of whether the band gap is direct or indirect, Theis<sup>30</sup> has suggested that the  $DX$  center emits electrons to the  $L$  valley only; since then the emission barrier will not depend on whether the lowest conduction band is at  $\Gamma$  or at  $X$ . A similar proposal has been suggested by Saxena.<sup>11</sup> However, we found that the pressure coefficient of  $E_e$  changed sign when the band gap changed from direct to indirect. Thus our results suggest that the emission barrier height is sensitive to the nature of the conduction-band minimum. The simplest explanation for this change in sign of  $dE_e/dP$  is that in the indirect-gap region the electron emits to a conduction-band minimum (presumably  $X$ ) different from the one it emits to when the band gap is direct (presumably  $\Gamma$  or  $L$ ). If we assume that the  $DX$  centers always emit electrons to the lowest conduction-band minimum, we expect that  $dE_e/dP$  will show a discontinuity at the  $\Gamma$ - $X$  crossover with a magnitude given by the difference  $dE_\Gamma/dP - dE_X/dP = 13$  meV/kbar. This is larger than the observed discontinuity in  $dE_e/dP$  of about 3.5 meV/kbar (with an uncertainty of about 20%) by more than a factor of 3. If we assume that, when the band gap is direct, the  $DX$  center emits electrons to the  $L$  valleys as proposed by Saxena and by Theis, then the discontinuity in  $dE_e/dP$  is reduced significantly to 7 meV/kbar. Although this is still larger than the observed value by a factor of 2, considering the experimental uncertainty we conclude that our results are roughly consistent with the Theis proposal when the band gap is direct. However, when the band gap is indirect the  $DX$  center emits to the  $X$  conduction-band minima. We note that a similar proposal has been suggested by Kaniewski and Kaniewska in explaining their results on the  $DX$  centers in  $\text{GaAsP}$  alloys.<sup>25</sup>

Using the relationship that the thermal ionization energy  $E_T = E_e - E_c$  we can determine the position of the  $DX$

center relative to the bottom of the conduction band of  $\text{Ga}_{1-x}\text{Al}_x\text{As}$  and hence also the energy of the  $DX$  center ( $E_{DX}$ ) relative to the valence band as a function of pressure. Although this indirect method results in larger errors in the values of  $E_{DX}$ , it allows us to compare our results with earlier measurements of  $E_{DX}$  from the Hall effect. The values of  $E_{DX}$  determined in this way are shown as solid squares in Figs. 6(a)–6(c) for the three alloys  $x=0.15$ , 0.25, and 0.35, respectively. The dashed lines drawn through the data points are least-squares fits to the data points. The pressure coefficients  $dE_T/dP$  determined in this way are tabulated in Table I. Shown on the same plots in Figs. 6(a)–6(c) are the variations of the  $\Gamma$ ,  $X$ , and  $L$  conduction-band minima with pressure. It is obvious that the pressure coefficients  $dE_T/dP$  in all three samples change from positive to negative at the direct- to indirect-band-gap crossover. Furthermore, in the direct-gap region the  $DX$  center follows approximately the  $L$  minima as noted by many authors. From Figs. 6(a)–6(c) we see that the pressure coefficient of  $E_{DX}$  is actually smaller than that of the  $L$  minima:  $dE_{DX}/dP \approx 0.8 dE_L/dP$  only. The most significant difference between alloying and pressure is in the behavior of  $E_{DX}$  near the direct- to indirect-band-gap crossover region. So far all the studies of the variation in the  $DX$  level with alloying have found no break in the dependence of the  $DX$  center energy on  $x$  near  $x_c \approx 0.4$ , where the band gap changes from direct to indirect. On the other hand, Saxena<sup>11</sup> has studied the pressure dependence of  $E_{DX}$  in  $\text{Ga}_{1-x}\text{Al}_x\text{As}$  using the Hall-effect measurement and found a change in the pressure coefficient of the  $DX$  center energy near the  $\Gamma$ - $X$  crossover. Saxena noted that the  $DX$  center seemed to follow the  $L$  level when the band gap was direct and the  $L$  and  $X$  minima when the band gap was indirect. Saxena deduced  $dE_T/dP$  to be  $-3.0$  meV/kbar in an  $x=0.23$  sample in the indirect-band-gap region in good agreement with our result in the  $x=0.25$  sample. Thus our results are in agreement with the earlier results of Saxena and support his proposal that the  $DX$  center has significant contribution from the  $X$  valleys in addition to the  $L$  valleys.

From the pressure-dependent values of  $E_T$  we have deduced the energy  $E_{DX}$  of metastable  $DX$  centers in  $\text{Ga}_{1-x}\text{Al}_x\text{As:Te}$  at ambient pressure. From a least-squares fit to our data we found  $E_{DX}$  increases approximately linearly with Al concentration (in the direct-band-gap region) as

$$E_{DX} = 0.802x + 1.547 \text{ eV} . \quad (5)$$

This result should be compared with the result of Chand *et al.*<sup>5</sup> in Si-doped  $\text{Ga}_{1-x}\text{Al}_x\text{As}$  where they obtained the expression  $E_{DX} = 0.54x + 1.57$  eV. We note that while in both cases the dependence of  $E_{DX}$  on  $x$  differs from that of the  $L$  conduction-band minima. Our value of  $dE_{DX}/dP$  for Te is larger than that of  $dE_L/dP$  while the corresponding value for Si is smaller. In an earlier measurement, Springthorpe *et al.*<sup>3</sup> have found that the dependence of  $E_{DX}$  in  $\text{Ga}_{1-x}\text{Al}_x\text{As:Te}$  on Al concentration followed exactly the  $L$  minima.

Recent studies on the pressure-dependent properties of

the  $DX$  centers have stimulated much activities in modeling the  $DX$  centers without invoking complex formation. Some of these models<sup>4,17,31</sup> attempted to depict the  $DX$  center as an effective-mass state of a donor with wave functions constructed from the  $L$  conduction-band minima only. These effective-mass models usually do not invoke large lattice relaxation of the donor atoms and therefore require *ad hoc* assumptions to explain the large

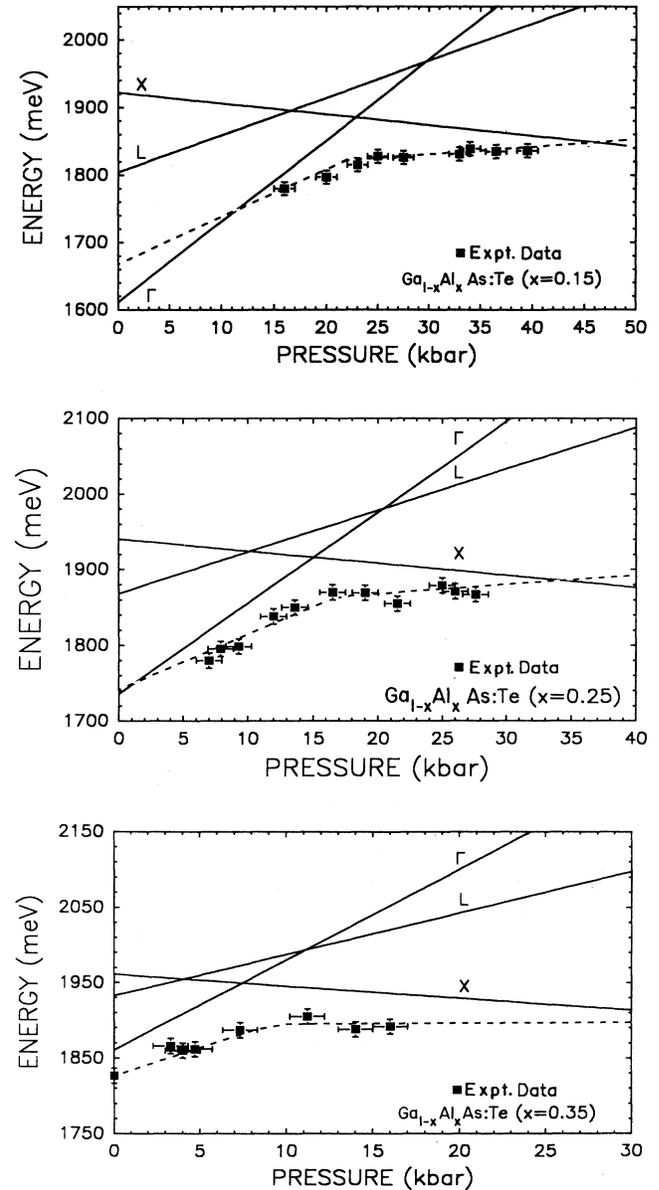


FIG. 6. Energy  $E_{DX}$  of the  $DX$  center relative to the top of the valence band for three  $\text{Ga}_{1-x}\text{Al}_x\text{As:Te}$  samples as a function of pressure: (a)  $x=0.15$  sample, (b)  $x=0.25$  sample, and (c)  $x=0.35$  sample. The dashed lines represent least-squares fits to the data. The variations of the  $\Gamma$ ,  $X$ , and  $L$  conduction-band minima are also shown as a function of pressure.

optical ionization threshold. There are also models with built-in large lattice relaxation such as the displaced donor-atom model proposed by Morgan.<sup>32</sup> This model used a tight-binding approximation to estimate the  $DX$  center energy and, so far, its predictions can be compared only qualitatively with experiment. Finally it has been proposed recently that  $DX$  centers are negative- $U$  centers.<sup>20,21</sup> In  $Ga_{1-x}Al_xAs$  with  $x > 0.25$  the ground state of the donor contains two electrons (to be denoted by  $DX^-$ ). In the model proposed by Chadi and Chang<sup>20</sup> (to be referred to as the CC model), if the donor (e.g., Si or Sn) is on a cation site, the  $DX^-$  state is formed by the donor atom undergoing large displacement along one of the tetrahedral bonds until it is almost planar with three As atoms in a threefold-coordinated geometry. For a donor on cation sites (such as Te) then one of its nearest-neighbor Ga atoms will undergo large lattice displacement.

So far Chadi and Chang<sup>20,33</sup> have applied their model to pure GaAs only where the  $DX^-$  level is metastable. Using *ab initio* self-consistent pseudopotential-total-energy calculations<sup>33</sup> they have calculated quantitatively many of the properties of the  $DX^-$  center. Many of their results such as the capture barrier height and optical ionization threshold are in good agreement with experiment. Furthermore, the large lattice displacement inherent in their model provided a satisfactory explanation for the large Stokes shift between the optical and thermal ionization energies in the  $DX$  centers. For this reason we will compare our results with the predictions of their model. In particular, Chadi and Chang proposed an expression for the pressure dependence of  $E_{DX}$  as

$$E_{DX}(P) = \left(\frac{1}{8}\right)[E_{\Gamma}(P) + 4E_L(P) + 3E_X(P)]. \quad (6)$$

Using the pressure coefficients for the conduction-band minima listed in Sec. III one obtains from Eq. (6) a pressure coefficient  $dE_T/dP \approx 8.4$  meV/kbar in the direct-gap region and  $\approx -5.2$  meV/kbar in the indirect-gap region. These results are qualitatively consistent with our results of  $dE_T/dP = 4.5-4.9$  meV/kbar in the direct-gap region and  $-1.7$  to  $-2.8$  meV/kbar in the indirect region. Perhaps the most significant difference between our results and the prediction of the CC model lies in the pressure dependence of  $E_{DX}$  as shown in Figs. 6(a)-6(c). In the CC model the  $DX$  center level is derived equally from all the states of the lowest conduction band taking into account only the degeneracy of the valleys at the  $\Gamma$ ,  $X$ , and  $L$  points of the Brillouin zone. As a result the  $DX$  center energy does not depend on which conduction-band valley has the lowest energy. We note that all the effective-mass models<sup>34</sup> based either on the  $L$  valleys only or on both  $L$  and  $X$  valleys produce the same conclusion. On the other hand, the experimental results show clearly that *the  $X$  conduction-band valleys start to exert a stronger influence on the  $DX$  center energy when the  $X$  valleys become the lowest conduction-band minima.* Saxena<sup>1</sup> has shown phenomenologically that this result can be explained by introducing a coupling between the  $L$  and  $X$

levels. Perhaps refinement in the CC model can explain the origin of this coupling.

Finally we note that most work on the  $DX$  centers has concentrated on Si-doped  $Ga_{1-x}Al_xAs$ .<sup>5,9,23,35</sup> Though the characteristics of the  $DX$  center in Si-doped samples are in general very similar to that of Te-doped samples, there are significant differences. For example, Lang *et al.*<sup>8</sup> have noted that the thermal and optical ionization energies of Si-induced  $DX$  centers were larger than those of Te-induced  $DX$  centers. Mooney *et al.*<sup>23</sup> and Calleja *et al.*<sup>9</sup> found that the activation energy for capture in Si-doped  $Ga_{1-x}Al_xAs$  samples varied by more than 200 meV when the Al concentration varied from 0.25 to 0.4. This variation is almost an order of magnitude larger than the variation of about 30 meV we found in Te-doped samples. Also the pressure dependence of the emission activation energy in Si-doped GaAs is different from what we found in this work. Both Mizuta *et al.*<sup>13</sup> and Li *et al.*<sup>15</sup> found that, in the direct-gap region,  $E_e$  decreases with pressure in GaAs:Si whereas we found that  $E_e$  increases with pressure. Other authors have also reported difference in behaviors between  $DX$  centers in  $Ga_{1-x}Al_xAs$  alloy system doped with S or Sn.<sup>8,12</sup> Thus one may conclude that these experimentally observed differences between  $DX$  centers derived from different donor species indicate a sensitivity in the  $DX$  center wave functions to some central cell effects which is not explained by all the proposed models.

## V. CONCLUSIONS

Deep-level transient spectroscopy and constant-temperature capacitance transient measurement have been used to study the emission and capture properties of  $DX$  centers in Te-doped  $Ga_{1-x}Al_xAs$  alloys as a function of pressure using a diamond-anvil high-pressure cell. In general the properties of  $DX$  centers in Te-doped  $Ga_{1-x}Al_xAs$  alloys were found to depend similarly on pressure and Al concentration. The pressure dependence of the  $DX$  center in  $Ga_{1-x}Al_xAs:Te$  in the direct-band-gap region is found to be different from that in the indirect-gap region. This dependence of the  $DX$  center properties on the symmetry of the lowest conduction band suggested that the  $X$  valleys play a significant role in the  $DX$  center properties contrary to the assumption of many models that only the  $L$  valleys are important.

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