Theory of the Atomic and Electronic Structure of *DX* Centers in GaAs and $Al_xGa_{1-x}As$ Alloys

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We propose that *DX* is a negatively charged defect center resulting from the "reaction" $2d^0 \rightarrow d^+ + DX^-$ where *d* represents a substitutional donor. The results of our pseudopotential calculations for Si- and S-induced *DX* centers in GaAs indicate large dopant-dependent relaxations leading to threefold-coordinated *interstitial* sites for either the donor or one of its nearest neighbors. A simple expression for the alloy composition and pressure dependence of the *DX* binding energy is suggested and used in an analysis of experimental data.

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The defect which gives rise to a deep donor level in $Al_xGa_{1-x}As$ alloys for $x \gtrsim 0.22$ is commonly known as the *DX* center.[1,2] The defect also appears in *n*-type GaAs when pressures in excess of 20 kbar are applied[3-8] or when the dopant concentration increases beyond $10^{19}/cm^3$ (Ref. 9). The *DX* center has a repulsive barrier for both electron emission *and* capture, leading to persistent photoconductivity. In addition, there is typically an order-of-magnitude difference between its $\simeq$0.1-eV thermal and $\simeq$1-eV optical ionization energies.[1,2,8] The large Stokes shift led Lang and coworkers[1,2] to propose that *DX* is a donor-defect complex which undergoes a large lattice relaxation. There is now strong evidence, however, that *DX* arises from a substitutional donor by itself.[3-9] This has led to suggestions that *DX* involves a displaced donor with either large[10-12] or, possibly, small[13] lattice relaxations.

In this Letter we propose new structural models for Si- and S-induced defect centers in GaAs derived from *ab initio* self-consistent pseudopotential calculations. The energetics of *DX* formation and its electronic structure are also examined and the results for GaAs are extended to the $Al_xGa_{1-x}As$ alloys with a simple model. The main conclusions from our calculations are the following:

(i) The *DX* center is a highly localized and negatively charged center resulting from the reaction

$$2d^0 \rightarrow d^+ + DX^-, \tag{1}$$

where d^0 and d^+ represent neutral and ionized fourfold-coordinated substitutional donors. The donors d^0 need not be spatially close to each other.

(ii) Defect formation involves a large bond-rupturing displacement of either the donor atom itself (for Si_{Ga}) or one of its nearest-neighbor Ga (or Al) atoms (for S_{As}) along a bond axis. In the following discussions, the notation *DX* is exclusively used to refer to the broken-bond configuration in order to distinguish it from the normal substitutional geometry denoted by *d*.

An immediate consequence of (i) is that *DX* should be electron-paramagnetic-resonance (EPR) inactive. To our knowledge, no EPR signal from *DX* has ever been reported in the literature. A recent study, with an enhanced sensitivity, by Khachaturyan, Weber, and Kaminska[14] has also failed to reveal any EPR activity and has led them to propose that a "negative *U*" defect center is responsible for both the lack of EPR and the persistent photoconductivity of *DX* centers.

In the following, we first examine a simple expression for the variation of the thermal binding energy of *DX* centers as a function of composition, pressure, and dopant concentration in $Al_xGa_{1-x}As$ alloys.

The thermal binding energy of a neutral *DX* center relative to the conduction-band minimum (CBM) is argued to vary with alloying (or with pressure) as

$$\Delta E_0(DX^0) = \Delta E_{\mathrm{CBM}} - \Delta E_{\mathrm{CB}}, \tag{2}$$

where E_{CBM} is the energy of the CBM and E_{CB} is the Brillouin-zone-averaged energy of the lowest conduction band, both measured relative to the valence-band maximum (VBM). The assumption behind Eq. (2) is that *DX* is a localized defect,[9] and the variation of its thermal occupancy level relative to the VBM, ΔE_{DX^0}, is nearly equal to ΔE_{CB}. Experimentally, only the variations of the energy bands at the Γ, *X*, and *L* points of the Brillouin zone are well known.[15] The Brillouin-zone average for ΔE_{CB} can be determined from these points with the approximation[16]

$$\Delta E_{\mathrm{CB}} \simeq \Delta[E(\Gamma) + 3E(X) + 4E(L)]/8. \tag{3}$$

The variations of the band edges in $Al_xGa_{1-x}As$ alloys are nearly linear in *x*, for $x \lesssim 0.6$, and the room-temperature values are given[15,17] by (in eV)

$$\begin{aligned} E(\Gamma) &\simeq 1.42 + 1.25x, \\ E(X) &\simeq 1.9 + 0.21x, \\ E(L) &\simeq 1.71 + 0.64x. \end{aligned} \tag{4}$$

Substitution in Eq. (3) yields

$$\Delta E_{\mathrm{CB}} \simeq 0.55 \Delta x. \tag{5}$$

Equation (4) indicates that for $x \lesssim 0.46$ the CBM is at

Γ, and for $x>0.46$ it is at the X point. Equations (2)-(5) therefore give

$$\Delta E_0(DX^0)=0.7\Delta x, \quad x\leq 0.46, \tag{6}$$

and

$$\Delta E_0(DX^0)=-0.34\Delta x, \quad x>0.46, \tag{7}$$

For a negatively charged center arising from Eq. (1), we need the variation of the energy of $DX^- + d^+$ relative to $2d^0$. If we use the same approach as before, this two-electron, two-site energy difference is expected to vary as

$$\Delta E_0(DX^-)=2\Delta(E_{\text{CBM}}-E_{\text{CB}})=2\Delta E_0(DX^0). \tag{8}$$

For a neutral center, the ratio of the densities of d^0 and DX^0 centers is equal to $\exp[-\beta E_0(DX^0)]$, where $\beta=1/kT$. For the DX^- center, however, it is $\frac{1}{2}E_0(DX^-)$ that enters the Boltzmann factor giving the relation between the densities of d^0 and DX^- centers. The reaction specified by Eq. (1) suggests that

$$(n_{d^0})^2=(n_{d^+})(n_{DX^-})\exp[-\beta E_0(DX^-)], \tag{9}$$

where n_i denotes the density of species i. If we use the relation $n_{d^+}\simeq n_{DX^-}$, Eq. (9) gives

$$\begin{aligned} n_{d^0}&=(n_{DX^-})\exp[-0.5\beta E_0(DX^-)]\\ &=(n_{DX^-})\exp[-\beta E_0(DX^0)]. \end{aligned} \tag{10}$$

The temperature dependence of the DX concentration, therefore, cannot be used to determine the charge state of DX. The experimentally derived binding energies,[15] which are based on a βE_0 dependence in the Boltzmann factor, need to be multiplied by 2 for a negatively charged state. To compare the predictions of the simple model to the experimental data of Chand *et al.*,[15] we will use the expressions for $\Delta E_0(DX^0)$ given by Eqs. (6) and (7) while keeping the factor of 2 for the case of a negative charge state in mind.

Equations (6)-(8) show that the binding energy of DX relative to the CBM increases with Al concentration until the direct-indirect band-gap transition at $x\simeq 46\%$ and then decreases. The predicted extremum of $x\simeq 46\%$ for the DX binding energy is in good agreement with the experimentally determined[3,15,18] range of $0.45\leq x\leq 0.48$. The 0.7-eV prefactor in Eq. (6) is nearly identical with the 707-meV value obtained by Chand *et al.*[19] from a best fit to their data. In this connection it is also interesting to look at the variation ΔE_{DX^0} of the DX thermal occupancy level *relative to the VBM* instead of the CBM. As discussed above in connection with Eq. (2), this variation is equal to ΔE_{CB} which from Eq. (5) is given by $0.55\Delta x$ for x in both the direct- and indirect-gap regimes. Since, from Eq. (4) the energy of the lowest conduction band at L varies as $0.64\Delta x$, the DX donor level, relative to the VBM, moves *as if* it were nearly tracking the L conduction state. The correlation between the motion of the two of $0.55/0.64\simeq 86\%$ is practically identical with the experimentally determined value[20] of $0.54/0.64\simeq 84\%$. This result shows that *the L-like variation of the DX energy in* $Al_xGa_{1-x}As$ *alloys can be explained without the assumption that it is an L-derived center.* The correlation between E_{DX} and $E(L)$ appears simply because the average energy of the lowest conduction band, E_{CB}, and therefore E_{DX^0} increase with alloy composition at nearly the same rate as the energy at the L point. The accuracy of Eq. (3) used in obtaining this result may be partially assessed by our noting that the lowest-order "special point" averaging gives $E_{\text{CB}}\approx E(L)$.[16] This indicates that the L-like variation of the DX binding energy is not limited to AlGaAs alloys alone, but should also hold approximately in other systems. Special care is needed to distinguish a genuinely L-derived effective-mass level from the more spatially compact DX state in these situations.

Making use of the *experimental* result that at $x\simeq 0.22$, the thermal binding energy of DX becomes equal to that of shallow donors ($\simeq 5$ meV), the integration of Eqs. (6) and (8) gives (in eV)

$$E_0(DX)=(0.7x-0.15)(1+q), \quad x\leq 0.46, \tag{11}$$

where q assumes the values of 0 or 1 for DX^0 and DX^-, respectively. Equation (11) predicts that DX is unbound (i.e., metastable) by $0.15(1+q)$ eV in GaAs. From Eqs. (2) and (8), a *charge-state independent* increase of 0.15 eV in $E_{\text{CBM}}-E_{\text{CB}}$ would be needed to stabilize DX in GaAs. One method for the realization of this increase is through the application of pressure. In this case the thermal binding energy E_0 is affected because of changes both in E_{CBM} and in the average energy of the conduction-band states E_{CB}. The pressure dependence of $E_0(DX)$ can be easily calculated. The pressure coefficients of the conduction-band states at the Γ, X, and L points for GaAs are well known[3,21] and, in meV/kbar, are equal to

$$\begin{aligned} &\delta E(\Gamma)/\delta P=12,\\ &\delta E(X)/\delta P\simeq -1.6,\\ &\delta E(L)/\delta P=5.5. \end{aligned} \tag{12}$$

A pressure of 18 kbar increases $E(\Gamma)$ by 216 meV and raises the average energy of the lowest conduction-band state, determined from Eq. (3), by 66 meV, resulting in a net change of 150 meV in $E_{\text{CBM}}-E_{\text{CB}}$ which should be sufficient to stabilize DX. This result is consistent with experimental results which show the appearance of DX centers in GaAs at pressures of about 20-30 kbar.[4-8] In the direct-gap region, the calculated pressure coefficient $\Delta E_0(DX)/\Delta P$ of 8.4 meV/kbar is consistent with experimentally determined values from pressure- and temperature-dependent Hall measurements[3,6] in GaAs and $Al_{0.15}Ga_{0.85}As$. In the indirect-gap regime, the pressure coefficient $\Delta E_0(DX)/\Delta P$ is calculated to be

−5.2 meV/kbar. The change in sign of the pressure coefficient and its overall magnitude are consistent with recent experimental results of Li *et al.*[22]

While the dependence of the *DX* binding energy on alloy composition or pressure does not allow us to infer its charge state, a comparison of the predicted and observed dopant-concentration dependence of the density of *DX* centers in GaAs provides strong evidence for a negatively charged center. For high dopant densities where the donor electrons form a degenerate electron gas, the formation of *DX* centers may occur either via the reaction $d^0+e \rightarrow DX^-$ for a negatively charged center, where e represents a free electron, or via $d^0 \rightarrow DX^0$ if *DX* were a neutral center. As discussed below the second reaction is energetically very unfavorable. The probability that an electron has sufficient energy to form a *DX* center is given by $\{1+\exp\beta(E_{DX}-E_F)\}^{-1}$, where E_F is the Fermi energy. At low temperatures, where $\beta(E_{DX}-E_F)\gg 1$, the stabilization of DX^0 or DX^-, relative to free electrons at E_F, requires a rise in E_F of 0.15 or 0.3 eV, respectively, relative to the CBM in GaAs. The variation of the *DX* concentration as a function of E_F, and therefore $E_{DX}-E_F$, has been determined by Theis, Mooney, and Wright.[9] From their experiments they conclude that E_{DX} lies $\simeq$0.28 eV above the CBM in GaAs. This is within 7% of the value expected from Eq. (11) for a negatively charged center and is significantly larger than the 0.15-eV value for a neutral center. A negatively charged *DX* center appears to be essential, therefore, in the reconciliation of the *DX* binding energy determined from the dopant-concentration measurements with those derived from the alloy-composition and pressure experiments. The problem of the pinning of the Fermi level in the conduction band by *DX* centers at high dopant concentrations is discussed in more detail elsewhere.[23]

We have carried out *ab initio* self-consistent calculations for Si and S substitutional donors in GaAs to examine in more detail the shallow-deep transition of donor levels in $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{As}$ alloys. Optimal atomic coordinates were determined from an iterative energy-minimization approach using a three-dimensionally periodic eighteen-atom unit cell. Our calculations show that in GaAs a neutral donor is stable against Jahn-Teller distortions. The local phonon mode of the $\mathrm{Si}_{\mathrm{Ga}}$ substitutional donor is calculated to be at $\simeq$334 cm^{-1} as compared to experimental values[24] of 379-384 cm^{-1}. The mode is found to be very anharmonic and the use of lattice distortions smaller than the 0.1 Å used in the calculations should improve the agreement between the theoretical and experimental values. For a negatively charged center, a metastable state with C_{3v} symmetry, which we associate with *DX*, is found. For a Si donor, the center involves a 1.17-Å motion of the Si atom away from one of its nearest neighbors, along its bond axis, into a threefold-coordinated interstitial position. For a S donor one of the nearest-neighbor Ga (or Al) atoms of the S dopant moves by 1.13 Å into an interstitial site. A donor-lattice bond is broken as a result of these atomic motions. The atomic distortions are nearly identical to those predicted to occur in the stable-to-*metastable* state transition of the *EL*2-related $\mathrm{As}_{\mathrm{Ga}}$-antisite defect in GaAs.[25]

The reaction represented by Eq. (1) is calculated to be energetically unfavorable by 0.22 ± 0.1 eV for both Si and S donors in GaAs. The surprisingly small value of the total-energy differences and the near equivalence of the results for Si and S are in qualitative agreement with the $\simeq$0.3-eV estimate from Eq. (11) and the 0.28-eV value derived from dopant-concentration experiments.[9] When the charge of the DX^- center is changed to DX^0 or DX^+, the interstitial atomic configuration is found to be highly unstable with respect to the ordinary fourfold-coordinated substitutional geometry and there is no barrier for the transformations to this geometry. The DX^0 to d^0 transition is calculated to be exothermic by $\simeq$1.3 eV.

Our calculations show that although the Si- and S-induced DX^- centers in GaAs are metastable, they have optically deep electronic levels associated with them. The optical ionization energies are calculated to be 1.05 eV for GaAs:Si and 0.74 eV for GaAs:S. The optical ionization energies are predicted to increase with pressure or alloying in $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{As}$. In the composition range where the band gap is direct (i.e., $x \le 0.46$), the optical gap is expected to vary as

$$\Delta E_{\mathrm{opt}} = \Delta E(\Gamma) - \Delta E_{\mathrm{CB}}, \qquad (13)$$

where the second term on the right-hand side represents the shift of the electronic level associated with *DX*. Substitution of Eqs. (4) and (5) in Eq. (13) gives $\Delta E_{\mathrm{opt}} = 0.70x$. The optical and thermal ionization energies are seen to have the same dependence on x and to be largest at $x \simeq 0.46$. The calculated results for GaAs together with Eq. (13) give an E_{opt} of 1.37 eV (1.06 eV) for Si-(S-) induced *DX* centers at $x = 0.46$. Since DX^0 is very unstable, the absorption of each photon by a DX^- center releases two electrons into the conduction band. For GaAs, our previous results on the pressure dependence of the conduction-band states used in conjunction with Eq. (13) predict, for GaAs:Si, a value of $E_{\mathrm{opt}} = 1.34$ eV for $P = 33$ kbar, which is in good agreement with the experimental value of 1.44 ± 0.04 of Li *et al.*[8] At higher pressures E_{opt} is expected to decrease because the CBM changes from Γ to X and the latter has a negative pressure coefficient.

The results of the pseudopotential calculations provide further insight into how the shallow-deep transition depicted by Eq. (1) takes place. The calculations show that when a neutral Si donor atom is displaced away from its nearest neighbor along a bond axis, the total energy increases as expected but the donor level becomes increasingly *deeper* as the displacement becomes larger.

When the level has dropped by more than the on-site Coulombic repulsive term U, which is calculated to be $\simeq$0.20–0.22 eV, the d^0 level can capture a free electron without expelling it immediately back into the CBM. At this point the formation of a d^- center leads to a further motion of the Si atom which transforms it into a DX^- center. The energy barrier for electron capture E_{cap} in lightly doped GaAs is calculated to be 0.55 ± 0.05 eV corresponding to the rise in energy for a 0.5-Å displacement of the Si atom. The barrier is expected to decrease linearly with E_{F} as the dopant concentration is increased. The Fermi level E_{F} in highly doped samples appears to get pinned at the point $E_0(DX^-)$ above the CBM where electrons at E_{F} can combine with d^0 centers, in the impurity band near the bottom of the conduction band, to form DX centers. If d^+ centers could be transformed to DX^- centers through the capture of two electrons, then E_{F} would be pinned at $\frac{1}{2}E_0(DX^-)$ or 0.15 eV above the CBM instead of the much larger observed value of 0.28 eV.[9]

In conclusion, from an analysis of experimental data on the composition, pressure, and dopant-concentration dependence of the DX binding energy in $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{As}$ alloys and from the results of *ab initio* pseudopotential calculations, we have presented evidence that DX is a negatively charged and highly localized defect center resulting from a large lattice distortion. A more detailed discussion of our results will be presented elsewhere.[23]

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