# Energetics of *DX*-center formation in GaAs and $Al_xGa_{1-x}As$ alloys

D. J. Chadi and K. J. Chang
*Xerox Palo Alto Research Center, 3333 Coyote Hill Road, Palo Alto, California 94304*

(Received 19 December 1988)

The energetics of the shallow-deep transition of donor states in $Al_xGa_{1-x}As$ alloys and the problem of Fermi-level pinning by *DX* centers in highly doped GaAs are examined via simple theoretical models and *ab initio* self-consistent pseudopotential total-energy calculations. The atomic displacements responsible for the formation of *DX* centers in Si- and S-doped GaAs are determined. Defect formation is found to be accompanied by a large bond-rupturing lattice distortion. The results of our pseudopotential calculations indicate that *DX* is a highly localized and *negatively* charged defect center. The atomic structure for *DX* is shown to provide a satisfactory explanation for the large Stokes shift between its optical and thermal ionization energies. An important conclusion of our study is that *DX* centers are an unavoidable feature of substitutional dopants and that the formation of these defects may be suppressed via the introduction of *interstitial* donors which are unlikely to undergo similar structural transformations. This implies that the normal doping procedure which relies on group-IV and -VI substitutional impurities needs to be modified. Possible choices for interstitial dopants from group-III and -V elements are examined.

## I. INTRODUCTION

Extensive experimental and theoretical work during the past decade on the electronic properties of group-IV (e.g., Si, Ge, and Sn) and -VI (e.g., S, Se, and Te) substitutional dopants in III-V ternary semiconductors, particularly in the $Al_xGa_{1-x}As$ alloy system, has led to many interesting hypotheses concerning the complexities exhibited by these donors.[1-44] The most important outcome of recent studies, is the realization that, independent of alloy composition, each donor gives rise to two types of electronic states:[4-28] a shallow and delocalized effective-mass level associated with the normal substitutional site configuration, and a more localized level, labeled *DX*, arising from a lattice distortion[45] at or near the donor.

In $Al_xGa_{1-x}As$ alloys the relative stability of the two types of states depends on alloy composition. For GaAs, and more generally for alloys characterized by $x \leq 0.22$, the shallow level with a binding energy of approximately 7 meV is more stable than the localized state which is a metastable resonance a few tenths of an eV above the conduction-band minimum.[4-13] For $x \geq 0.22$, the localized *DX* state is no longer a resonance. It is a bound state which is more stable than the shallow donor state, and its binding energy reaches a maximum of $\approx 160$ meV at the direct-indirect band-gap transition point.[13] The stability of the *DX* resonances in $Al_xGa_{1-x}As$ alloys with $x \leq 0.22$ can be increased through the application of pressure.[5-9] Each kilobar of pressure has, very crudely, the same effect on the band structure and on the relative stabilities of *DX* versus shallow donor states as a one-percentage-point increase in $x$. The shallow-deep transition in GaAs occurs at pressures of about 20–30 kbar, with the pressure for inducing the transition decreasing with increasing Al content. The pressure experiments[5-9] have been crucial in demonstrating that the shallow-deep transition of the electronic levels is associated with the donor atom itself and that an association of the donor with other defects such as an As vacancy[1-3,31] to produce the *DX* center is an unlikely event.

An important characteristic feature of the *DX* center is the existence of a repulsive barrier for the transformation of a shallow state into the localized *DX* state for all alloy compositions.[1-15] The total energy of the donor-host system has, therefore, two minima as a function of the local atomic environment of the donor. As a result, the *DX* center in $Al_xGa_{1-x}As$ alloys (for $x \geq 0.22$) exhibits a persistent photoconductivity effect.[1-3] Using a simple configuration-coordinate diagram of the type shown in Fig. 1, Lang *et al.*[1-3] showed that the measured barriers for electron capture (from a shallow state into a *DX* center) and for emission (from a *DX* center into a shallow state) led to the prediction of a large optical gap $E_{\text{opt}}$ of 1.1 eV for the *DX* center which was in good agreement with their experimental result of 1.2 eV. They attributed the large Stokes shift of $\simeq 1$ eV between the thermal and optical ionization energies of the *DX* center to a large lattice relaxation. Results from the most recent optical[14,15] and pressure[8] experiments strongly favor the large lattice-relaxation model. The prevailing theoretical view now is that *DX* formation involves a lattice distortion at or around the donor atom.[21-27,44]

In this paper we present a more detailed discussion of the results of a recently published theoretical study of the atomic and electronic structure of *DX* centers in GaAs and $Al_xGa_{1-x}As$ alloys.[26] As in our earlier work, we approach the problem of the *DX* center in two complementary ways. In Sec. II we propose a simple expression for the composition[13,37,38] and pressure dependence[5-9] of the binding energy of *DX* centers in $Al_xGa_{1-x}As$ alloys. The major conclusion drawn from this analysis is that the much discussed correlation between the *DX* and $L$ conduction-band-minimum energies[13,32,35] can be satisfactorily explained without invoking an $L$-derived

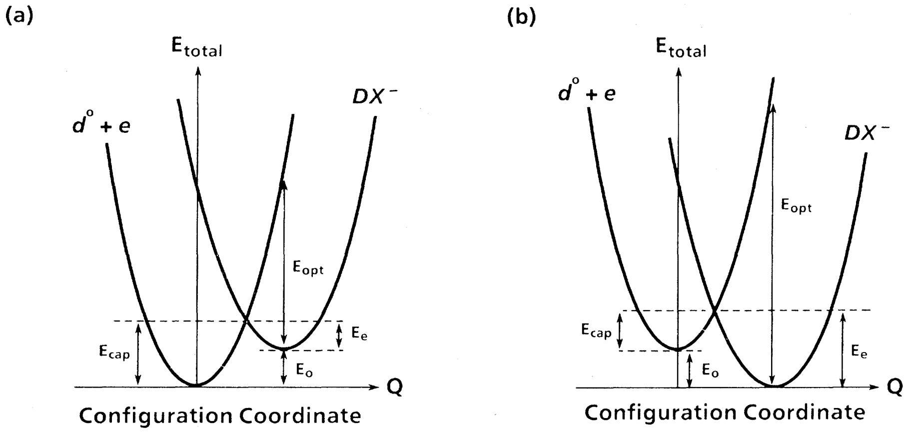

FIG. 1. Configuration-coordinate diagrams for *DX* centers in GaAs and typical $Al_xGa_{1-x}As$ alloys are shown in (a) and (b), respectively. The *DX* center is a metastable resonance in GaAs and has a higher energy than a shallow donor state ($d^0$). For $Al_xGa_{1-x}As$ alloys characterized by $x \geq 0.22$, *DX* centers are more stable than the shallow donors.

effective-mass level.[36]

In Sec. III we address the structural, energetic, and electronic aspects of Si- and S-induced *DX* centers in GaAs using an *ab initio* self-consistent pseudopotential approach. The results of these calculations indicate that *DX is a strongly localized* and *negatively charged defect* which behaves as a negative-*U* center (see *Note added in proof*).[26] The negative-*U* aspect of the model has been independently suggested in other work.[16,27] The calculated atomic structure for *DX* is shown to be characterized by a very large dopant-dependent lattice relaxation leading to donor-host bond breaking (see Fig. 2). In addition, the large Stokes shift between the thermal and optical binding energies and the barriers for electron capture and emission are shown to be properly accounted for by the predicted structural models for Si- and S-induced *DX* centers.

The results of Secs. II and III are used in Sec. IV to suggest that the formation of *DX* centers is associated with structural transformations which are specific to substitutional donors and unlikely to occur for interstitial donors. The advantages and disadvantages of using particular interstitial dopants are examined. A summary of the main results of this paper is given in Sec. V.

## II. THERMAL BINDING ENERGY OF DX CENTERS

### A. Charge state of *DX* centers

In the nondegenerate doping limit, the *DX* center is proposed to result from the following set of reactions:[26]

$$d^0 \rightarrow d^+ + e \; , \tag{1}$$

which costs only $\simeq 7$ meV, and

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

which involves the capture of a free electron. The two reactions add up to give

$$2d^0 \rightarrow d^+ + DX^- \; . \tag{3}$$

In Eqs. (1)–(3) *d* represents a normal fourfold-coordinated *substitutional* donor, *DX* denotes the broken-bond configurations shown in Fig. 2, *e* denotes a free electron in the conduction band, and the superscripts specify the charge states. The neutral donors in Eq. (3) are not necessarily in close spatial proximity of each other to form $DX^-$. Equation (3) indicates that the density of *DX* centers should, at most, equal one-half the density

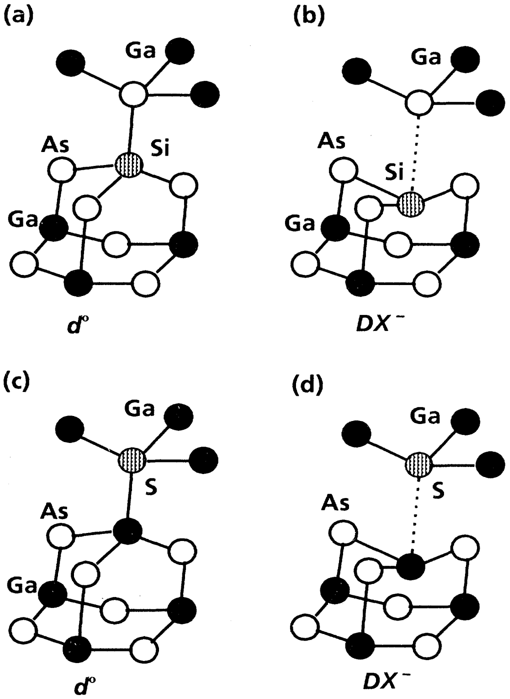

FIG. 2. Schematic views of the normal substitutional sites and the broken-bond configurations giving rise to the *DX* centers in Si- and S-doped $Al_xGa_{1-x}As$ alloys are shown (a)–(d). A comparison of (b) and (d) shows that the lattice relaxations leading to *DX* formation are dopant dependent.

of the donor atoms. This will hold if there is no other shallow donor which is itself stable against a *DX*-like transformation, but which can act as a reservoir to supply the free electrons needed to drive the donors in Eq. (3) into the *DX* state. As discussed in Sec. III, *both* $DX^0$ and $DX^+$ *are found to be completely unstable with respect to* $d^0$ *and* $d^+$, respectively, i.e., the energies of $DX^0$ and $DX^+$ states are significantly higher than those of the $d^0$ and $d^+$ states, and there is *no energy barrier* for the transformations between these structures. This is the reason why the reaction in Eq. (3) is not written in the form $2DX^0 \rightarrow DX^+ + DX^-$.

Equation (3) suggests that *DX* should behave as a negative-*U* defect center.[26,27] If the ground state is a singlet state, then *DX* should have no electron-spin-resonance (ESR) activity. The results of three recent experiments[27,33,34] which have not found any ESR signal from the *DX* center are consistent with a negative-charge state for this defect. Higher sensitivity measurements may be needed, however, to confidently rule out a paramagnetic ground state for the *DX* center. (See *Note added in proof.*)

In highly doped samples[9,10] where the electrons form a degenerate gas and the donors are nearly all ionized, *DX* formation may occur from the capture of *two* electrons by an ion:

$$d^+ + 2e \rightarrow DX^- . \tag{4}$$

The atomic distortions responsible for the formation of *DX* involve a large lattice displacement which leads to the breaking of a donor-lattice bond. *The notation DX is used exclusively in this paper to refer to the broken-bond configurations shown in Fig. 2.* The consequences of Eqs. (1)–(4) for the properties of *DX* centers are analyzed in the following sections. The dependence of the binding energy of *DX* centers on alloy composition, pressure, and dopant concentration as a function of its charge state is examined below.

### B. Binding energies of $DX^0$ and $DX^-$ centers

In this section we present a more detailed discussion of a previously proposed expression for the variation of the thermal binding energy $E_0$ of *DX* centers with pressure or alloying.[26] Even though our *ab initio* calculations show that when neutral, the *DX* structure is totally unstable with respect to the normal fourfold-coordinated donor $d^0$, it is instructive, nevertheless, to examine the dependence of the binding-energy variation of a *DX* center as a function of its charge state. For a neutral center the binding energy $E_0(DX^0)$ relative to the conduction-band minimum (CBM) in $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{As}$ alloys is proposed to vary with alloying as[26]

$$\Delta E_0(DX^0) = \Delta E_{\mathrm{CBM}} - \Delta E_{\mathrm{CB}} , \tag{5}$$

where $E_{\mathrm{CBM}}$ is the energy of the CBM and $E_{\mathrm{CB}}$ is the average over the Brillouin zone (BZ) of the energy of the lowest conduction band, both energies being measured relative to the valence-band maximum (VBM). The idea underlying Eq. (5) is based on the experimentally derived inference that *DX* is a localized defect[10] and that as a result its wave function should be derived, approximately equally, from *all* the states of the lowest conduction band. As a result the variation of its thermal occupancy level, $\Delta E_{\mathrm{DX}^0}$, *relative to the* VBM is given by

$$\Delta E_{\mathrm{DX}^0} \simeq \Delta E_{\mathrm{CB}} . \tag{6}$$

The assumption of a strongly localized *DX* used in Eqs. (5) and (6) is supported by the electronic charge-density calculations, shown in Figs. 3–5, for our recently proposed structural model for this defect. In writing Eq. (6) we are implicitly assuming that the impurity potential is not strong enough to cause a mixing of the higher-lying conduction bands. Exceptions to Eq. (6) can arise when the difference between the potentials of the host and impurity atoms is sufficiently large to cause an appreciable mixing of other conduction (or possibly valence) bands. The symmetry of the deep center may also play an important role in determining the actual mix of the conduction-band states.

The assumption that *DX* is derived equally from all the states of the lowest conduction band implies

$$\Psi_{DX} \simeq \sum_{\mathbf{k}} e^{ic(\mathbf{k})} \Psi_{\mathbf{k}} , \tag{7}$$

where $\Psi_{\mathbf{k}}$ is a Bloch function solution of the periodic lattice for the first conduction band with wave vector $\mathbf{k}$ and $c(\mathbf{k})$ is an arbitrary *real* number. This expression for $\Psi_{DX}$ is reminiscent of the definition for a Wannier func-

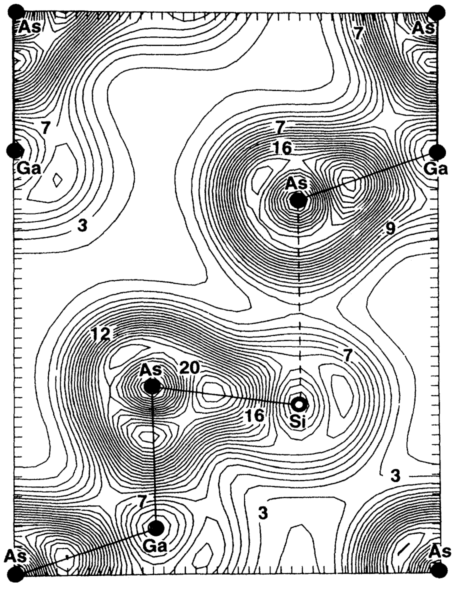

FIG. 3. The *total* valence-electronic charge density of GaAs, including the contribution from a fully relaxed and occupied Si-induced $\mathrm{DX}^-$ level, is shown in a $(1\bar{1}0)$ plane. The broken Si—As bond is shown as a dashed line. The Si atom has two additional bonds pointing into and out of the plane of the paper. The vertical and horizontal directions are along the cubic [111] and $[11\bar{2}]$ axes, respectively. The contour lines are in units of electrons per bulk GaAs unit-cell volume.

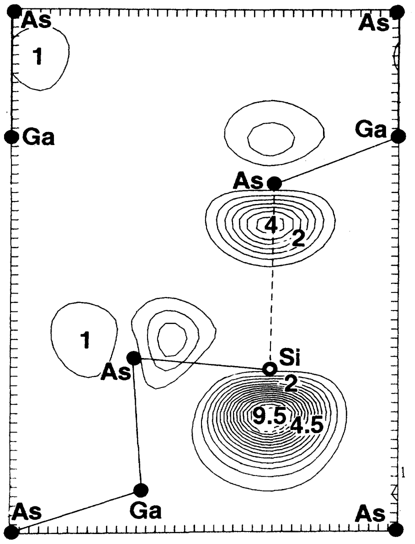

FIG. 4. The charge density for the deep donor state associated with the $DX^-$ center in Si-doped GaAs is shown. This state corresponds to the normally occupied one in $\mathrm{Al}_x\mathrm{Ga}_{1-x}$ alloys for $x \geq 0.22$.

tion $w(\mathbf{r}-\mathbf{R})$ localized at site $\mathbf{R}$ of the lattice:

$$w(\mathbf{r}-\mathbf{R})=\sum_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{R}}\Psi_{\mathbf{k}} \ . \tag{8}$$

If the values of the $c(\mathbf{k})$ are known, we can define new Bloch functions $\Phi_k=\exp[ic(\mathbf{k})]\Psi_{\mathbf{k}}$ which include the phase factors $\exp[ic(\mathbf{k})]$ in their definition and then construct new Wannier functions according to Eq. (8) with $\Psi_k$ replaced by $\Phi_k$. For this special case, $\Psi_{DX}$ is equal to the Wannier function centered at the origin. For the general case, however, $\Psi_{DX}$ is a linear combination of Wannier functions localized at various sites.

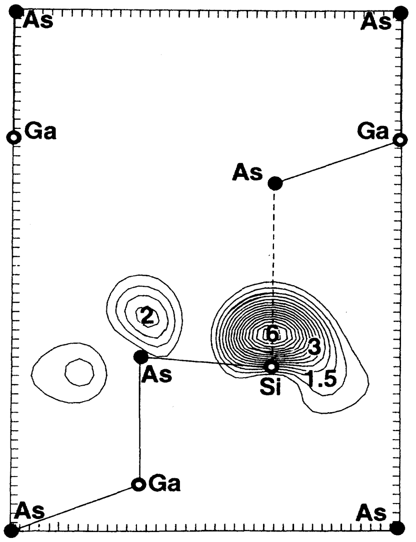

FIG. 5. The charge density associated with the empty state associated with the $DX^-$ center for Si-doped GaAs and $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{As}$ alloys is shown.

The energy of the neutral $DX$ center for the particular choice of wave function made in Eq. (7) is given by

$$E_{DX^0}=E_{\mathrm{CB}}+\langle\Psi_{DX}|U|\Psi_{DX}\rangle \ , \tag{9}$$

where $E_{\mathrm{CB}}$ is the BZ-averaged energy of the first conduction band and $U$ is the perturbation potential introduced by the impurity. Since $\Psi_{DX}$ is very localized, the last term in Eq. (9) is a measure of the central-cell contribution to the energy of $DX$. The consistency of Eqs. (6) and (9) requires that the variation of this term with alloying should be small. Our results for the charge density of the Si-induced $DX$ center in GaAs, shown in Figs. 3–5, suggest that this should be a satisfactory approximation because of the highly localized nature of the charge distribution. Experimentally, the local environment is observed to make a small but measurable difference in the energy of the $DX$ center.[41,42]

The BZ average of the conduction-band energies needed to determine $\Delta E_{\mathrm{CB}}$ in Eq. (6) can be carried out in a number of ways. The most direct method is to use a fine mesh of points in reciprocal space for the averaging. A much simpler approach is to use the "special-points" approach which relies on a few well-chosen representative points. The hierarchy of the special-point sets for fcc Bravais lattices appropriate for GaAs and $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{As}$ alloys has been previously determined.[46] The desired average can be determined with high accuracy as the number of special points used in the sampling is increased. A zeroth-order approximation to the average energy is $\Delta E_{\mathrm{CB}} \simeq \Delta E(L)$.[46] A more accurate approximation, which is discussed in the Appendix, is obtained by using the energies at the $\Gamma$, $X$, and $L$ points according to the prescription

$$\Delta E_{\mathrm{CB}} \simeq \Delta[E(\Gamma)+3E(X)+4E(L)]/8 \ . \tag{10}$$

This is a very convenient formula for determining $\Delta E_{\mathrm{CB}}$ since the variations in the band-edge energies with alloying, pressure, and temperature are well known. The variations of the band edges in $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{As}$ alloys are nearly linear in $x$ for $x \leq 0.6$ and at room temperature are given (in eV) by[13]

$$E(\Gamma) \simeq 1.42+1.25x \ , \tag{11}$$

$$E(X) \simeq 1.90+0.21x \ , \tag{12}$$

and

$$E(L) \simeq 1.71+0.64x \ , \tag{13}$$

The variation with alloying of the BZ-averaged energy of the lowest conduction band obtained from Eqs. (10)–(13) is given by

$$\Delta E_{\mathrm{CB}} \simeq 0.55\,\Delta x \ . \tag{14}$$

The three-point $\Gamma,X,L$ averaging gives a variation of $E_{\mathrm{CB}}$ with $x$ which is only 86% of the rate of the corresponding change of $E(L)$ instead of being equal to it when the zeroth-order approximation $\Delta E_{\mathrm{CB}} \simeq \Delta E(L)$ is used.

Equations (11)–(13) show that the CBM is at $\Gamma$ for $x \leq 0.46$ and at the $X$ point of the BZ for $x > 0.46$. Equations (5)–(14) therefore predict

$$\Delta E_0(DX^0) = 0.7\,\Delta x,\quad x \leq 0.46 \tag{15}$$

and

$$\Delta E_0(DX^0) = -0.34\,\Delta x,\quad x > 0.46\ . \tag{16}$$

For a negatively charged center arising from Eq. (3) we need the variation of the energy of $DX^- + d^+$ relative to $2d^0$. Using the same approach as above, this difference is equal to

$$\Delta E_0(DX^-) = 2\Delta(E_{\rm CBM} - E_{\rm CB}) = 2\,\Delta E_0(DX^0)\ . \tag{17}$$

For a neutral center the densities of $d^0$ and $DX^0$ are related by

$$n_{d^0} = n_{DX}\exp[-\beta E_0(DX^0)]\ , \tag{18}$$

where $\beta = 1/kT$ and $T$ is the absolute temperature. 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. (3) suggests that

$$(n_{d^0})^2 = n_{d^+}(n_{DX^-})\exp[-\beta E_0(DX^-)]\ , \tag{19}$$

where $n_i$ denotes the density of species $i$. When $n_{d^+} \simeq n_{DX^-}$, Eq. (19) gives

$$\begin{aligned} n_{d^0} &= (n_{DX^-})\exp[-0.5\beta E_0(DX^-)] \\ &= (n_{DX^-})\exp[-\beta E_0(DX^0)]\ . \end{aligned} \tag{20}$$

The ratio $n_{d^0}/n_{DX}$ determined from Eqs. (18) and (20) is independent, therefore, of the charge state of $DX$. The experimentally derived binding energies[13] which are based on a $\beta\Delta E_0$ dependence in the Boltzmann factor need to be multiplied by 2 for a negatively charged state. In the following, in order to compare the predictions of the simple model with the experimental data of Chand *et al.*,[13] we use the expressions for $\Delta E_0(DX^0)$ given by Eqs. (15) and (16). The factor-of-2 difference between $\Delta E_0(DX^0)$ and $\Delta E_0(DX^-)$ states should be borne in mind, however.

Equations (15) and (16) 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 it decreases. The predicted extremum of $x \simeq 46\%$ for the $DX$ binding energy is in good agreement with the experimentally determined[13,37,38] range of $0.45 \leq x \leq 0.48$. The 0.7-eV prefactor in Eqs. (15) for $x < 0.46$ is nearly identical with the 707-meV value obtained by Chand *et al.*[13] from a best fit to their data. The variation above $x = 0.46$ is also in very good agreement with experimental data.

Equations (6), (13), and (14) show that the thermal occupancy level $E_{DX}$ relative to the VBM varies as if it is tied to the $L$ point of the conduction band. The correlation between the motion of the two, as measured by the ratio of the coefficients of $\Delta x$ in Eqs. (13) and (14), is $\frac{0.55}{0.64} \simeq 86\%$. This is very nearly the same as the measured correlation coefficient[13] of $\frac{0.54}{0.64} \simeq 84\%$. The derivation of this result makes it clear, however, that *the L-like variation of the DX energy*[13,35] *can be explained without the assumption that it is an L-derived effective-mass level.*[36] The correlation between $E_{DX}$ and $E(L)$ appears because $\Delta E_{DX} \simeq \Delta E_{\rm CB}$ and $\Delta E_{\rm CB} \approx \Delta E(L)$. If $DX$ were an $L$-derived effective-mass level, then $\Delta E_{DX}$ would have to be *exactly*, and not merely approximately, equal to $\Delta E(L)$. Such an exact relationship between the $DX$ and $E(L)$ energy levels has not been experimentally established. In addition, an $L$-derived level, even when intervalley scattering is accounted for, is a much more delocalized defect than is experimentally observed to be the case for $DX$.[10] Since the special-points-derived relation $\Delta E_{\rm CB} \approx \Delta E(L)$ is material independent, the correlation $\Delta E_{DX} \approx \Delta E(L)$ is not restricted to $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{As}$ alloys, but should hold approximately in other materials.

Other expressions for the alloy dependence of the band energies discussed by Theis[47] and Aspnes[48] lead to essentially the same results. For the new parametrization schemes one also finds that the use of $\Delta E_{DX} \simeq \Delta E_{\rm CB}$ together with the three-point averaging scheme of Eq. (10), results in $\Delta E_{DX} \simeq 0.84\,\Delta E(L)$ or $\Delta E_{DX} \simeq 0.77\,\Delta E(L)$. This shows that $E_{DX}$ is, for all reasonable parametrizations, most strongly correlated with $E(L)$.

### C. Pressure dependence of the *DX* binding energy

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, the integration of Eqs. (15) and (17) gives (in eV)

$$E_0(DX) = (0.7x - 0.15)(1+q),\quad x \leq 0.46 \tag{21}$$

where $q$ assumes the values of 0 or 1 for $DX^0$ and $DX^-$, respectively. Equation (21) predicts that $DX$ is unbound (or metastable) by $0.15(1+q)$ eV in GaAs. From Eqs. (5) and (17) a charge-state-independent increase of 0.15–0.17 eV (depending on the extrapolation used[10]) in $E_{\rm CBM} - E_{\rm CB}$ is needed to stabilize $DX$ in GaAs. One method for inducing this increase is through the application of pressure. The pressure dependence of $E_0(DX)$ can be easily calculated under the assumption that the contribution of the last term in Eq. (9) to the pressure coefficient is small. The pressure coefficients of the conduction-band states at the $\Gamma$, $X$, and $L$ points for GaAs are well known[49] and, in meV/kbar, are equal to

$$\delta E(\Gamma)/\delta P = 12\ , \tag{22}$$

$$\delta E(X)/\delta P \simeq -1.6\ , \tag{23}$$

and

$$\delta E(L)/\delta P = 5.5\ . \tag{24}$$

An approximate estimate for the pressure dependence of $E_{\rm CB}$ evaluated using Eq. (10) and Eqs. (22)–(24) is

$$\delta E_{\rm CB}/\delta P \simeq 3.6\ ; \tag{25}$$

therefore, using Eq. (12),

$$\delta[E(\Gamma)-E_{\mathrm{CB}}]/\delta P \simeq 8.4 \ . \tag{26}$$

The required (0.15–0.17)-eV increase in $E(\Gamma)-E_{\mathrm{CB}}$ needed to stabilize the *DX* center in GaAs translates to a pressure of 18–20 kbar. This result is consistent with experimental data 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 the experimentally determined values from pressure- and temperature-dependent Hall measurements[9,37] in GaAs and $\mathrm{Al}_{0.15}\mathrm{Ga}_{0.85}\mathrm{As}$ and with other recent measurements[8] which give values in the range 6–7.5 meV/kbar. In the indirect-gap regime the pressure coefficient $\Delta E_0(DX)/\Delta P$ is calculated to be $-5.2$ meV/kbar.[8] The change in sign of the pressure coefficient and its magnitude are also consistent with recent experimental results.[8]

The $\Gamma,X,L$- averaging scheme can also be used to determine the approximate temperature dependence of the *DX* binding energy since the shifts of the energies of the band-edge states with temperature are well known, particularly for GaAs.[48] The temperature shifts of the $\Gamma$, $X$, and $L$ conduction states with respect to the VBM have the same sign and are nearly equal to each other in GaAs. This implies that $E_0(DX^0)$ in GaAs should be approximately temperature independent.

### D. Fermi-level pinning position in heavily doped GaAs

If *DX* were a neutral center resulting from the reaction

$$d^{+}+e \rightarrow DX^{0} \ , \tag{27}$$

then the probability that an electron would have the minimum energy necessary to form a *DX* center would be given by

$$f(E_{DX^0})=[1+\exp\beta(E_{DX^0}-E_F)]^{-1} \ , \tag{28}$$

where $E_F$ is the Fermi energy. At low temperatures where $\beta(E_{DX^0}-E_F) \gg 1$ the stabilization of $DX^0$, relative to free electrons at $E_F$, would require a rise in $E_F$ of approximately 0.15 eV relative to the CBM in GaAs, according to Eq. (21). The *DX* centers would, in fact, lead to a pinning of the Fermi energy at 0.15 eV above the CBM because they would become energetically as favorable as the free-electron states at this value of $E_F$. The variation of the *DX* concentration as a function of the dopant density and, therefore, as a function of $E_F$ has been determined by Theis, Mooney, and Wright.[10] From their experiments they conclude that at the highest doping level $E_{DX}$ lies $\simeq 0.28$ eV above the CBM in GaAs. This is nearly twice the value for a neutral center suggested by Eq. (21) from an extrapolation of the alloy composition dependence of the $DX^0$ binding energy to GaAs. The experimental results on the Fermi-level–pinning position may appear, at first, to agree with the prediction of Eq. (21) for a negatively charged *DX* center. However, the two-electron reaction given by Eq. (4) suggests that the required minimum energy *per electron* to form a $DX^-$ center is only one-half as large as $E_0(DX^-)$ and should be equal to 0.15 eV, as in the case of the neutral center. This implies that $E_F$ should be pinned at 0.15 eV above the CBM, independent of the charge state of the *DX* center. An explanation for the experimentally observed[9,10] higher pinning position of $E_F$ is provided below.

The energy of the *DX* resonance above the CBM is experimentally observed to increase slightly with dopant density in the high-doping regime in GaAs.[10] A very small increase ($\simeq 1$ meV) in the *DX* energy is expected from Eq. (7) when the sum over the conduction-band states is restricted to be over only the unoccupied states. This is due to the fact that even at the highest doping levels,[9,10] e.g., $n_0=1.8\times10^{19}$ cm$^{-3}$, the volume of $k$ space occupied by the free electrons is extremely small. The shifting $E_{DX}$ with respect to the CBM is mainly due to band-gap renormalization in heavily doped semiconductors resulting from the Coulombic interactions between the electrons. One effect of this renormalization is a lowering of the energies of the states near the $\Gamma_1$ conduction band which will show up as an effective increase in the position of the *DX* level with respect to the CBM. The appropriate size of the reduction in the energy of the $\Gamma_1$ state is given by[50]

$$\Delta E(\Gamma_1)=-\frac{2e^2k_F}{\pi\epsilon}-\frac{e^2\lambda}{2\epsilon}\left[1-\frac{4}{\pi}\tan^{-1}\left[\frac{k_F}{\lambda}\right]\right] \ , \tag{29}$$

where $k_F=(3\pi^2 n_0)^{1/3}$ is the Fermi wave vector of the electrons in the conduction band, $\epsilon$ is the dielectric constant of the material ($\epsilon \simeq 10.9$ for GaAs), and $\lambda=(6\pi n_0 e^2/\epsilon E_F)^{1/2}$ is the Thomas-Fermi screening parameter. For the case of highly doped GaAs where $n_0 \simeq 1.8\times10^{19}$ cm$^{-3}$ and $E_F$ is 0.28–0.29 eV above the CBM,[9,10] the first term in Eq. (29) gives a downward shift of the conduction band of about 68 meV, while the other terms in the large square brackets give an upward shift of 11 meV. The total shift of 57 meV provides a partial explanation for why the measured pinning position of the Fermi level in GaAs is at a higher energy than the 0.15-eV value extrapolated from the binding energy in $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{As}$ alloys. Another factor affecting how high $E_F$ can be raised without creating *DX* centers is the attractive interaction between the conduction electrons and the ionized $d^+$ impurity centers. The magnitude of this interaction has been estimated to be[50]

$$\Delta E \simeq -\frac{4\pi n e^2}{\epsilon a^* \lambda^3} \ , \tag{30}$$

where $a^*=\epsilon\hbar^2/m^*e^2$ is the effective Bohr radius and $m^*$ is the density of states effective mass. For $n_0=1.8\times10^{19}$ cm$^{-3}$, the conduction-electron–impurity interaction in Eq. (30) gives a correction of nearly 50 meV to the stability of the free electrons. In the highly doped materials there is an additional contribution affecting the stability of a *negatively* charged defect center. For this case the Coulombic interaction between the $DX^-$ center and the free electrons raises the energy of this center relative to its value in intrinsic GaAs. The magnitude of this interaction is estimated to be about 25–45 meV. The three corrections—57 meV from the lowering of the conduction-band energy, 50 meV from the electron-impurity interaction, and 25–45 meV from the $DX^-$-conduction-electron interaction—together amount to 130–150 meV, which is sufficient to provide an explanation for why the observed Fermi-level–pinning position[9,10] with respect to the CBM in heavily doped GaAs samples is $\simeq 0.14$ eV higher than the 0.15-eV value expected from an extrapolation of the *DX* binding energy in $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{AS}$ alloys to GaAs.

## III. RESULTS OF *AB INITIO* PSEUDOPOTENTIAL CALCULATIONS

A brief description of our *ab initio* self-consistent calculations for Si and S substitutional donors in GaAs was given in Ref. 26. Calculations for $d^0$, $d^+$, $DX^0$, $DX^+$, and $DX^-$ structural states were each done separately using an 18-atom $\sqrt{3}\times\sqrt{3}\times\sqrt{6}$ hexagonal supercell with its *c* axis oriented along the [111] axis. Although the unit cell is relatively small, it is still sufficiently large to provide reliable information on the structural properties of *DX* centers. The same unit cell was used in our previous study of the *EL*2 defect center in GaAs.[51] The results obtained in that case for the charge-density distributions and structural properties of the antisite were found to be in good accord with similar calculations employing a 54-atom cell.[52] For the present study, the band dispersion of the donor state from the zone center to the Brillouin-zone edge, resulting from the use of a finite-sized cell, is calculated to be 0.2 eV. The local phonon vibration mode for the Si on Ga-site donor is calculated to be nearly 340 $\mathrm{cm}^{-1}$ as compared to the experimental values[53] of 379–384 $\mathrm{cm}^{-1}$. Our calculations indicate that the mode is quite anharmonic.

The optimal atomic coordinates were determined by minimizing the total energy. Hellmann-Feynman forces were calculated and utilized in the optimization process. Our calculations show that a *neutral* donor is stable against Jahn-Teller distortions in GaAs. The major result of our calculations is, however, that a metastable state with a large lattice relaxation leading to a broken-bond configuration (Fig. 2) and a $C_{3v}$ symmetry is possible for a *negatively* charged center. As discussed below, we find that this center has many of the properties associated with the *DX* center. For a Si donor, the distortion leading to *DX* formation involves a 1.17-Å motion of the Si atom away from one of its nearest-neighbor As atoms, along the bond axis, into a threefold-coordinated interstitial position. The bonding configuration for the Si atom changes from $sp^3$ to $sp^2$ as a result of the relaxation. This is best seen by the 118.4° angles about the Si atom in the interstitial configuration. The threefold-coordinated As atom resulting from the Si displacement relaxes outward, reducing its angles from 109.47° to 106.5°. Electronic charge is transferred from the Si atom to the As atom in this process. Maximal bond-length changes of $-2.4\%$ between Ga and As atoms near the Si donor are found. 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 position. A sulfur-gallium bond is broken as a result of this relaxation. The bond angles about the threefold-coordinated Ga (or Al) atom are calculated to be 118.3° and those around S about 112°. Maximal bond-length changes of $+2.8\%$ between Ga and As atoms are found for this case. The atomic distortions in Fig. 2 are nearly identical to those predicted to occur in the *metastable* state of the *EL*2-related $\mathrm{As}_{\mathrm{Ga}}$ antisite defect in GaAs.[51] The valence-electron charge density for a Si-induced $DX^-$ center is shown in Fig. 4. The charge is primarily concentrated on the Si donor atom, but there is a significant amount of charge on the threefold-coordinated As atom resulting from the bond rupture.

The reaction represented by Eq. (3) is calculated to be energetically unfavorable by $0.22\pm0.1$ 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. (21). 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.

The proposed $C_{3v}$ symmetry for the *DX* center is in agreement with the theoretical predictions of Morgan.[21] More recently, he has shown that the variations of deep-level transient-spectroscopy signals from Si-induced *DX* centers in $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{As}$ alloys as a function of alloying[43] can be explained by a structural model in which the donor atom goes into an interstitial position, bringing it into relatively close contact with neighboring cations, which can be either Ga or Al.[44] The $C_{3v}$ symmetry is also consistent with the experimentally derived symmetry from phonon transmission measurements.[17] These experiments show a trigonal symmetry for Sn-doped samples and an orthorhombic or trigonal symmetry for Te-doped ones. Other experiments based on analyses of extended x-ray-absorption fine structure (EXAFS) have also provided information on the local atomic environment of *DX* centers.[18,19] The EXAFS results of Sette *et al.*[19] for S-doped GaAs show that there are two types of atomic environments around the S atoms. One-half of the S atoms are found to be in their normal substitutional positions, but the local environment of the other half is found to be severely distorted. This picture would be in good agreement with our predictions for S-induced *DX* centers if one-half of the S atoms are in *DX* states and the other half are in ionized fourfold-coordinated $d^+$ states. This would mean that a very large fraction of the donors are in *DX* centers where, normally, these defects are not stable except at very high doping levels. Mizuta and Kitano[18] using the same technique infer a very small lattice relaxation for the case of Se. More recently, Mössbauer spectroscopy has been applied to Sn-doped samples, and the results seems to indicate a significant local distortion of atoms around Sn.[20] More extensive experimental tests are needed to resolve the discrepancies between the various experimental data and to determine whether *DX* centers, in fact, involve large lattice relaxations.

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. These values are significantly larger than the 0.22-eV thermal ionization energies of the corresponding *DX* centers. The calculated large Stokes shift between the two ionization energies as well as the difference in the optical gaps between Si- and S-induced *DX* centers are in good agreement with experimental data. When $DX^-$ is stable, the absorption of each photon is predicted to release *two* electrons into the conduction band because $DX^0$ is highly unstable, transforming immediately to a $d^+$ state, releasing one electron into the conduction band.

We now address the problem of the capture barrier for the shallow-deep transition of donor states. The pseudopotential 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 Coulomb 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 $E_{\text{cap}}$ in lightly doped GaAs is calculated to be $0.55\pm0.05$ eV, corresponding to the rise in energy for a 0.5-Å displacement of the Si atom. Combining this with the result of the total-energy calculation which shows that *DX* is unstable by $\simeq 0.22$ eV with respect to shallow donors in GaAs, the emission barrier is estimated to be $0.33\pm0.1$ eV. These results are consistent with recent experimental data.[43] However, the data show that the capture barrier height in $\text{Al}_x\text{Ga}_{1-x}\text{As}$ alloys varies strongly with composition and has a minimum at $x=0.35$.[43] Within the model discussed above, the capture barrier would be expected to be approximately constant since the bonds affected most by the Si motion are Si—As ones. Electron capture via an intermediate level, as discussed by Theis[28] (e.g., through an antibonding donor-host level) may be important in describing the capture process and needs further examination.

## IV. ELIMINATION OF *DX* CENTERS

### A. Substitutional versus interstitial donors

The results of the *ab initio* pseudopotential calculations discussed in the preceding section show that the formation of a *DX* center and the concomitant shallow-deep transition of the donor level in *n*-type GaAs is accompanied by a bond-breaking distortion at a *substitutional* donor site. The question naturally arises, therefore, whether the creation of *DX* centers can be inhibited through the use of donor atoms which give rise to shallow levels but which are not susceptible to the same type of lattice instability. The possibility of replacing substitutional donors with interstitial ones which do not form strong bonds with their surrounding atoms comes to mind. This indicates that the conventional doping procedure which relies on the introduction of atoms from column IV or VI of the Periodic Table into the lattice needs to be modified or possibly abandoned. There are many possible choices for interstitial doping of $\text{Al}_x\text{Ga}_{1-x}\text{As}$ alloys. In the following group-V and -III elements are considered.

### B. Interstitial As atoms

Recent calculations of Baraff *et al.*[54] suggest that an interstitial As atom has an electronic level which lies above the CBM in GaAs and which, therefore, empties its electron into the conduction band. This electronic level structure provides an explanation for why the isolated As interstitial, if present in GaAs, has not been detected via electron-spin-resonance experiments. Optically detected electron-nuclear double-resonance experiments[55] provide, however, strong evidence for the presence of As interstitials in GaAs samples grown in an As-rich environment.[56] The presence of As interstitials may provide a simple explanation for the large enhancement in the room-temperature free-carrier density observed by Basmaji *et al.*[39] in $\text{Al}_x\text{Ga}_{1-x}\text{As}$ alloys grown by metal-organic vapor-phase epitaxy under a very high $p_{\text{As}}/(p_{\text{Ga}}+p_{\text{Al}})$ partial pressure ratio of 95. The samples in this experiment were doped with Sn which, according to our theory, will actually tend to *reduce* the free-electron concentration arising from the As interstitial atoms because of its tendency to form *DX* centers in high-Al-content alloys. A preliminary analysis of recent experimental results[57] in our laboratory indicates that donors not susceptible to *DX*-like instabilities, which we believe arise from As interstitials, can be introduced into $\text{Al}_x\text{Ga}_{1-x}\text{As}$ alloys with a high Al content with densities of about $(2-3)\times10^{17}$ $\text{cm}^{-3}$. In these samples the free-carrier density is observed to *decrease* with increasing Si impurity content in $\text{Al}_x\text{Ga}_{1-x}\text{As}$ alloys with high Al densities and to increase with it when the Al content is low.

The use of a high As flux during growth can lead to the formation of As antisites in addition to As interstitials. The As antisite defect is known to be a (deep) donor, so it should not interfere with the *n*-type doping resulting from interstitial arsenic atoms.

### C. Interstitial Al, Ga, and B

Interstitial group-III dopants have three valence electrons, two of which are in low-energy *s* states and would lie below the VBM in $\text{Al}_x\text{Ga}_{1-x}\text{As}$ alloys, and the other is a *p* electron with an energy that, in the limit of weak interactions with neighboring atoms should fall several eV above the CBM of GaAs, for Ga and Al, and near the CBM for B.[58] An interstitial atom is, in general, strongly interacting with its neighbors. The *ab initio* self-consistent calculations of Baraff and Schlüter[59] show, however, that *interstitial* Ga does, in fact, behave as a donor and not an acceptor in GaAs. These group-III atoms, particularly Ga and Al, would be, therefore, ideally suited for *n-type* doping if they can be introduced into interstitial sites. A potential problem with trying to incorporate these atoms into the lattice via ion implantation is the possibility of forming substitutional cation antisites which will behave as double acceptors in *n*-type materials, thereby compensating the donor electrons arising from the interstitial atoms. However, Ga antisites should be statistically balanced by other donor-type defects. For example, the creation of an As-interstitial, As-vacancy pair will lead to *n*-type behavior since the As-interstitial and As-vacancy defects are individually donor-type defects.[59] A Ga-vacancy defect would be an acceptor, and it would have a high probability of annealing out as a result of recombination with either Ga- or As-interstitial atoms. The formation of energies for these defects is very sensitive to $E_F$, with acceptorlike defects becoming energetically more favorable in *n*-type samples and vice versa.[59] Despite the potential complications of introducing interstitial donors, and the equally important question of the stability of these donors, the possibilities for this type of doping procedure are very intriguing and deserve more critical experimental investigations.

The only group-III atom which has been examined so far for its effect on *DX* centers is boron. The experiments of Li *et al.*[60] show that incorporation of B in Si-doped GaAs leads to two new donor levels with reduced emission and capture activation energies (compared to *DX* centers). The experiments were carried out at pressures of 20–30 kbar, where *DX* is ordinarily more stable than shallow donors. A similar effect has not yet been found in an $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{As}$ alloy.[60] The fact that normal *DX* centers are observed to vanish with the introduction of B could be indicative of B-Si complex formation,[60,61] which prevents the Si atom from going into the threefold-coordinated interstitial position necessary for *DX* formation. Since the concentration of the B impurities in the samples studied[60] was at least twice that of Si, the possibility of interstitial B atoms which are not interacting with any Si atoms cannot be discounted. A different possible explanation involving charge transfer between Si and B but no direct interaction between these atoms is considered in the following.

We have done self-consistent pseudopotential calculations on interstitial B in pure GaAs and have tested two different interstitial positions for which the nearest neighbors of B are either all Ga ($T_{d1}$) or all As atoms ($T_{d2}$). We find that for the relaxed structures the most stable site for B, in either neutral or negative-charge states, is at the $T_{d2}$ site, whereas for a positive-charge state it is at the $T_{d1}$ site. The energy differences between the two sites are nearly 0.2 eV for $\mathrm{B}^0$, 0.4 eV for $\mathrm{B}^-$, and 0.2 eV for $\mathrm{B}^+$. Combining the results of our calculations for B with those for Si, we find that the reaction

$$DX^- + \mathrm{B}^0 \to d^0 + \mathrm{B}^- , \tag{31}$$

in which a Si-induced $DX^-$ center is transformed into a neutral substitutional dopant $d^0$ altering the charge state of an interstitial B atom at $T_{d2}$ which is not necessarily close to the Si atom, does not cost any energy. A direct interaction between a *DX* center and B may not be needed, therefore, for *DX* to become unstable in the presence of boron. Since $DX^-$ is more stable than $d^0$ at the high pressures at which the experiments are done, the combination of Eqs. (3) and (31) suggests that the overall reaction

$$DX^- + 2\mathrm{B}^0 \to d^+ + 2\mathrm{B}^- \tag{32}$$

may be exothermic under pressure. This would lead to a complete disappearance of *DX* centers when the B-interstitial concentration is at least equal to the Si concentration. It should be emphasized again that this reaction does not depend on having the B and Si atoms in close proximity to each other. A boron concentration in excess of that of Si (or other donors) would lead to the presence of $\mathrm{B}^0$ in addition to $\mathrm{B}^-$ interstitials in GaAs, unless B is a negative-*U* center.[62,63] The experiments of Li *et al.* showing the presence of two different boron-induced donor levels in Si-doped GaAs could be associated with the two charge states of boron interstitials. The *DX*-like emission and capture barriers exhibited by B may be related to the energy differences between various interstitial positions favored by B as a function of its charge state. More detailed studies are obviously needed to answer the questions raised by the experimental data.

## V. CONCLUSIONS

In conclusion, 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 were analyzed using a simple theoretical model. The results of our *ab initio* pseudopotential calculations on Si- and S-induced *DX* centers in GaAs indicate that *DX* is a negatively charged and highly localized negative-*U* defect center (see Fig. 4) which results from a large dopant-dependent lattice distortion. We propose that the large, bond-breaking, lattice relaxations (shown in Fig. 2) responsible for deep-electron-trap formation by *DX* centers are relevant to *substitutional* donors only and that it should prove possible to reduce the concentration of these defects by introducing *interstitial* dopants which do not undergo the same type of atomic displacements. The possibilities of using various group-III or -V elements for this purpose were examined.

Metastable broken-bond *DX*-type defects are also expected to be present in group-IV and other group-III–V semiconductors. Whereas the defect can be stabilized relative to a shallow donor by pressure in some III–V compounds, such as GaAs, for which the energy of the conduction band can be increased with pressure, this approach will not be successful for a group-IV semiconductor such as Si because of the negative pressure coefficient of the lowest conduction band at the *X* point of the Brillouin zone. It may be possible to stabilize the defect through alloying, however, in a way similar to the situation in $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{As}$ alloys.

*Note added in proof.* The results of very recent high-sensitivity magnetic-susceptibility measurements by K. Khachaturyan, D. D. Awschalom, J. R. Rozen, and E. R. Weber (unpublished) indicate that the *DX* center may have a paramagnetic ground state. For the negatively charged center, such as the one discussed in this paper, this would imply that the ground state is associated with a triplet and not a singlet state as implicitly assumed here. By the Pauli exclusion principle, two distinct electronic orbitals would be needed to form the triplet state. The charge-density distribution shown in Fig. 4 suggests that these orbitals are localized on the threefold-coordinated Si and As atoms resulting from *DX* formation. The observation of a paramagnetic state can be compatible, therefore, with a negative charge state for the *DX* center. More experimental and theoretical work remains to be done to obtain a better estimate of the singlet-triplet–state energy difference.

## ACKNOWLEDGMENTS

We would like to thank M. L. Cohen, C. B. Duke, C. Herring, J. Kakalios, R. M. Martin, T. Theis, E. Weber, and P. Y. Yu for useful discussions. This work was supported in part by the U.S. Office of Naval Research through Contract No. N00014-82-C-0244.

## APPENDIX

In this Appendix the use of the $\Gamma,X,L$-averaging scheme for determining the Brillouin-zone average of the conduction-band energy is examined in more detail. The special-point-averaging method is based on the fact that the energy $E(\mathbf{k})$ of the conduction band can be expanded in a Fourier series:

$$E(\mathbf{k})=E_{\mathrm{CB}}+\sum_n h_n e^{i\mathbf{k}\cdot\mathbf{R}_n} , \tag{A1}$$

where $\mathbf{R}$ is a (nonzero) lattice vector. The Brillouin-zone average of $E(\mathbf{k})$ is just the first term in the expansion, $E_{\mathrm{CB}}$. Using the symmetry properties of $E(\mathbf{k})$ for a zinc-blende lattice, the expansion can be written out as

$$E(\mathbf{k})=E_{\mathrm{CB}}+\sum_n f_n \sum_{|\mathbf{R}|=C_n} e^{i\mathbf{k}\cdot\mathbf{R}} , \tag{A2}$$

where the lattice vectors have now been grouped into symmetry-related shells with $C_{n+1}\geq C_n\geq 0$. The coefficients $f_n$ are related to the symmetrized combinations of the matrix elements of the Hamiltonian between Wannier functions centered at the origin and at lattice sites $\mathbf{R}=\mathbf{C}_n$. When the band under consideration varies smoothly with $\mathbf{k}$, $f_n$ drops rapidly in magnitude as $C_n$ becomes large. In such a case, $E(\mathbf{k})$ can be represented by a few terms of the Fourier series and the coefficients $f_m$ corresponding to lattice vectors larger than a critical radius $C_{\max}$ can be ignored. The special-points method evaluates $E_{\mathrm{CB}}$ by using a combination of $\mathbf{k}$'s and weighting factors such that the phase factors $e^{-i\mathbf{k}\cdot\mathbf{R}}$ cancel each other for $R\leq C_{\max}$. The $\Gamma,X,L$ averaging leads to a cancellation of the first three terms in Eq. (34) corresponding to the $(\frac{1}{2}\frac{1}{2}0)$, (100), and $(1\frac{1}{2}\frac{1}{2})$ groups of fcc lattice vectors. This means that if the $\mathbf{k}$ dependence of the conduction band in the $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{As}$ alloys can be reproduced by using only the first three Fourier coefficients $f_n$ in Eq. (34) (actually *all* the coefficients for which the phase factors add up to zero), then the average obtained from these points will be accurate. The problem of interest in Sec. II is the evaluation of the variation in $E_{\mathrm{CB}}$ as a function of alloy composition and not $E_{\mathrm{CB}}$ itself. The Brillouin-zone average obtained from the use of a small sampling mesh generally comes out more accurately for the variation than for $E_{\mathrm{CB}}$ itself, largely as a result of a cancellation of errors.

The zeroth-order approximation $E_{\mathrm{CB}}\simeq E(L)$ mentioned in Sec. II is valid if the only appreciable Fourier coefficients are $f_{1/2\,1/2\,0}$ and $f_{1\,1/2\,1/2}$ and the intermediate coefficient $f_{100}$ can be ignored. The single Baldereschi point[64] (0.622, 0.295, 0) works well when $f_{1/2\,1/2\,0}$ and $f_{100}$ are nonzero, and higher coefficients can be left out. The optimal two-point scheme with $\mathbf{k}_1=(\frac{1}{4}\frac{1}{4}\frac{1}{4})$ and $\mathbf{k}_2=(\frac{3}{4}\frac{1}{4}\frac{1}{4})$ with weighting factors of $\frac{1}{4}$ and $\frac{3}{4}$, respectively, works well when the energy band can be accurately represented by the first *seven* Fourier expansion coefficients in Eq. (34) corresponding to the $(\frac{1}{2}\frac{1}{2}0)$, (100), $(1\frac{1}{2}\frac{1}{2})$, (110), $(\frac{3}{2},\frac{1}{2},0)$, (111), and $3(\frac{1}{2}\frac{1}{2}0)$ lattice vectors of the primitive fcc lattice and when $f_{200}$ and higher coefficients are negligible. More accurate schemes for the evaluation of Brillouin-zone averages are discussed in Ref. 46.

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