PHYSICAL REVIEW B VOLUME 34, NUMBER 4 15 AUGUST 1986

Theory of the *DX* center in $Al_xGa_{1-x}As$ and GaAs crystals

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(Received 2 April 1986)

It is argued that (1) the so-called "*DX* center" is a simple substitutional donor which is displaced from its normal, centered, lattice position, (2) its deep state is derived from a triplet of symmetry T_2, not A_1 as is generally assumed, and (3) the donor displacement, driven by the energy of an occupied antibonding orbital, resembles a strong Jahn-Teller effect but differs because of the large potential barrier between the centered (T_2) donor state and the distorted deep state. This model provides a natural explanation for the bulk of the data published on *DX* centers, especially the large barrier for thermal capture and the far-infrared absorption spectra reported by Theis *et al.* for the $1s$-$2p$ transition in Si-doped $Al_xGa_{1-x}As$. The far-infrared absorption spectra indicate that the lowest state of symmetry A_1 lies where it is expected, about 70 meV below the L conduction-band edge, or nearly 100 meV *above* the deep "*DX*" level.

INTRODUCTION

There is, at present, no satisfactory explanation for the unusual properties exhibited by so-called "*DX* centers" in n-type $Al_xGa_{1-x}As$ crystals.[1-3] The persistent photoconductivity (PPC) at low temperatures, the large barriers for thermal capture and ionization into and out of the deep donor states, and the large threshold for photoionization all support the suggestion by Nelson[1] and by Lang and Logan[2] that for $x > 0.2$ the donor ground state involves a large lattice relaxation. In a later paper[4] Lang, Logan, and Jaros proposed, in order to account for such a large effect, that there may be another unknown defect associated with and coupled to the donor—possibly an As vacancy. Hence, the name "*DX*" had been assigned to the (presumed) composite defect.

Two objections to the complex model are immediately apparent: (1) Essentially all of the donor atoms incorporated into the crystals are electrically active as *DX* centers,[1,5] suggesting that any associated defect must be readily available at a small energy cost. (2) All of the observed effects are qualitatively similar[6,7] for donors of different species—the group-IV donors Si, Ge, and Sn on the group-III sublattice and the group-VI donors S, Se, and Te on the As sublattice—suggesting that the *DX* center does not involve a site-selective defect (such as an As vacancy).

An even more compelling objection to this model has appeared recently in the Japanese work showing than n-type GaAs crystals under 20—30 kbar of hydrostatic pressure exhibit PPC (Ref. 8) and a DLTS peak[9] similar to those in $Al_xGa_{1-x}As$ with $x = 0.2$ to 0.3—confirming that *DX* centers are also present in GaAs and become the ground state when the pressure exceeds about 20 kbar. This result provides strong evidence that (1) the *DX* properties are associated with isolated donors, not with complexes involving the donor and some unknown associate and (2) the appearance of the deep state is a consequence of the band (or bond) structure of the semiconductor, modified by pressure or alloying, and is not due primarily to the inhomogeneity of the crystals.

In spite of numerous ingenious experiments which have been performed, many misconceptions and misinterpretations of these and of their theoretical basis have persisted. In this article I attempt to rectify some of these misinterpretations and to derive the properties expected for an isolated donor in such materials. I show, further, that the interpretation of the published experimental results in the light of this analysis leads directly to a simple and adequate model.

THE THEORY OF DONOR STATES

The potential acting upon an electron in the field of a positively charged donor ion can be conveniently separated into two parts—the attractive long-range (screened) Coulomb potential and the local (central-cell) potential associated primarily with the central ion and its near neighbors. The long-range potential alone is sufficient to generate a great number of bound states, but of these only a few (the deeper states) have a large enough overlap with the central cell to be significantly perturbed by its potential. For these reasons we study first the deepest states (of each symmetry) in the effective mass (EM) approximation and then ask what the consequences of the central-cell potential on these states should be.[10]

In the absence of the short-range potential there is a set of well-defined localized states associated with each of the minima (valleys) of the conduction band. These sets are only weakly coupled by the Coulomb potential, so that the energies depend mainly on the band masses.[11-13] Thus, there is a series of "hydrogenic" EM states ($1s$, $2s$, $2p$, etc.) associated with each of the conduction band valleys—one at Γ, three at X (neglecting any small effects of the six valley "camel's back" structure suggested in Ref. 14), and four at L. Only the lowest of these, the $1s$ states, are expected to overlap and, hence, to be perturbed significantly by the central potential,[15] although mixing among any states having the same point symmetry will occur if they are sufficiently close in energy. Thus, we begin by investigating the seven 1*s* EM states.

(1) The 1*s* state derived from Γ is shallow, near 10-meV deep,[11] and so has a very small amplitude at the donor. It shows little perturbation by the central cell, although there can be a weak mixing with other states of symmetry A_1, if they lie near the same energy.

(2) The 1*s* state associated with a single X valley is of moderate depth, about 40 meV (Ref. 11). The effect of the central potential in mixing and perturbing the three degenerate $1s(X)$ states depends on whether the donor occupies a group-III or a group-V site, because the electron wave function in the lowest valley at X is *even* about an As site but is *odd* about Ga (Ref. 16). Silicon donors replace Ga (or Al), so that the three 1*s* states transform like *p* functions and are *not mixed* by the central potential. Thus, they are triplets, of point symmetry T_2 in the T_d group, and the 1*s* states bound to Ge and Sn behave in the same way. The one-valley functions around an As-site donor, however, are *s* like (even). Hence, the impurity potentials close to the group-VI donors S, Se, and Te *do mix* the three valley functions and lower the symmetric (A_1) combination to a depth of about 100 meV leaving a doublet (E) state near the EM energy.[17] Of these only the A_1 state overlaps the central potential appreciably. The E-state wave functions vanish at the origin and also, because of the valley symmetry, are small along the $\langle 111 \rangle$ bond directions toward the nearest-neighbor atoms.

(3) A 1*s* state derived from an L valley is also of moderate depth, probably about 25 meV.[11] The impurity potential does mix the valleys, however, so that a symmetric A_1 state is pulled down an additional 25 meV or so by the attractive central potential, leaving behind a triplet T_2 state near its one-valley value. The difference between this T_2 state derived from L and the T_2 or E state derived from X is that, although the wave functions of all three vanish at the origin, only those derived from L are very sensitive to the potential at the $\langle 111 \rangle$ nearest-neighbor bonds. We shall find that this allows a new, and most important, interaction.

We wish to show that most of the observed properties of the *DX* centers can be understood in terms of these seven states.[10]

THE PROPERTIES OF *DX* CENTERS

The *DX* centers are easily observed only in $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{As}$ alloys having $x \geq 0.22$, or in GaAs under pressures over about 20 kbar. For lower Al concentrations, $x < 0.2$, the band gap remains direct, as in GaAs, with the lowest conduction band minimum lying at the Γ point in the center of the Brillouin zone. The lowest donor states in this composition range are shallow, as in GaAs, and are bound by only a few meV.[11]

With increasing x, however, the direct gap increases rapidly (by about 12 meV for each percent Al content), and the Γ minimum crosses, for alloy compositions $x \gtrsim 0.22$, a highly localized donor state which becomes the ground state. It is this deep state which has been most often identified with the *DX* center, although in this latter composition range electrons bound to the donors can occupy either the shallow or the deep states. The fact that a donor could bind an electron in either of these has caused much confusion, because the shallow and deep states were often assumed to arise from different defects.[18] That this is not generally the case was clearly established by the work of Theis *et al.*[19]

A striking consequence of there being two kinds of states, and of the fact that electrons can make capture transitions between the two only with great difficulty, is the appearance of PPC. PPC appears at low temperatures when electrons in the deep state are excited (for example, optically) into the shallow donor states. Because of their small binding energies these shallow states are always partially ionized and exhibit conductivity, except at the lowest temperatures and at very small donor concentrations. What is odd is that at temperatures below 77 K the electrons remain in the Γ states for hours, or even days,[2] and are not captured into the lower-energy deep states unless the temperature is raised enough to excite them over a barrier of several hundred meV.[20] This fact suggests that transitions between the two states involve a large lattice relaxation and, as I discuss below, put strict conditions on the potential energy curves associated with this relaxation.

Various attempts have been made to understand the energy of the deep state through a model based on EM theory, as I have done above, but to treat this state as a composite of the 1*s* bound states derived from the Γ, L, and X band edges.[21,22] These calculations, however, have generally ignored the symmetries of the states and tacitly assumed that all were A_1.[22] As noted above this is not true for group-IV donors. That the deep state is probably also not derived from EM A_1 states is demonstrated by the far-infrared (FIR) absorption experiment performed by Theis *et al.*[19] and described in the following section.

THE 1*s*-to-2*p* FIR ABSORPTION

The deep Si donor state is known to lie above the shallow 1*s* state derived from the Γ valley in GaAs but to *cross* it in $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{As}$ and to become the ground state when x exceeds ~ 0.22. The shallow $1s(\Gamma)$ state is known to be of symmetry A_1, so that, if the deep state were also of A_1 symmetry, this crossing would produce an observable mixing. In their experiment Theis *et al.*[19] follow the absorption peak associated with the 1*s*-to-2*p* transition in the shallow (Γ) bound states as x increases from 0 (GaAs) to about 0.34. (See Fig. 1.) The energies of this peak are shown in the inset in Fig. 1. The transition energy increases from 4.5 meV (in GaAs) to about 14 meV (for $x = 0.34$) and appears to change smoothly, at first gradually, but then more rapidly for x above 0.27. There is no indication of an anticrossing at small x, although additional data should be taken between $x = 0.15$ and $x = 0.27$, but the rapid increase of the energy above 0.27 indicates an anticrossing near $x = 0.37$ which has depressed the $A_1(\Gamma)$ initial state, as the figure shows. (The 2*p* level cannot move above the band edge.[23]) Such an anticrossing can occur if there is an excited A_1 state lying about 90 meV above the deep ground state, approximately where the A_1 state derived from L is expected, and which, as x increases, mixes with the rising shallow 1*s* level, thus depressing its energy. The lines in Fig. 1 are

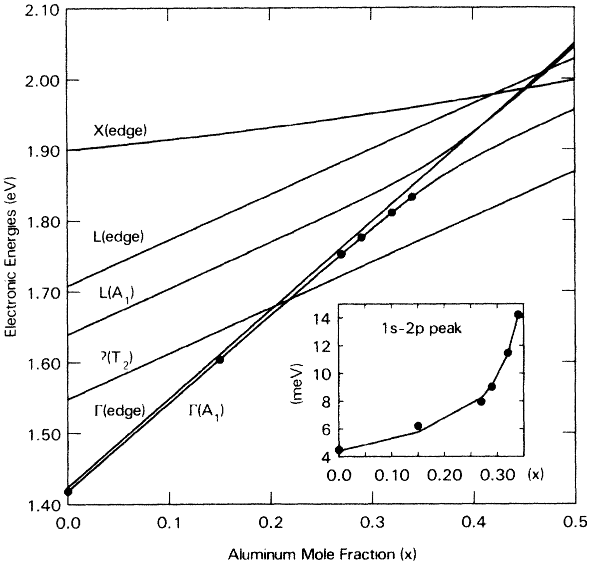

FIG. 1. The band-edge energies and the fit to the FIR absorption data. The deep state, drawn 160 meV below the L edge, is in good agreement with experiment for this range of x. The insert shows the energy of the $1s$-to-$2p$ FIR absorption band peak. The points are measured (Ref. 19), and the line is a calculated fit based on published values of the band edges (Ref. 24) and two parameters—the matrix element of mixing, $V=15$ meV, and the depth of the $L(A_1)$ state below L, $E_A=70$ meV. This places the crossing at $x=0.37$. The experimental uncertainty, not shown, increases with x and approaches ±3 meV at $x=0.34$.

a fit of these data to a possible band-edge energy diagram for the alloy.[24,25] At the larger values of x this A_1 state lies so far below the shallow $1s$ level that the lowest (mixed) A_1 state contains little $1s$ character. Hence, the transition becomes weak and very broad, and the peak disappears. These effects were apparent in the FIR experiment and are responsible for the absence of data for $x>0.34$.

The FIR results, when interpreted in terms of the EM-derived states discussed above,[26] lead to two important conclusions. (1) The A_1 state derived from the L conduction band valleys is not deeply bound but lies about where it is expected from conventional theory. (2) Another state, which the discussion above suggests is related in some way to the T_2 state derived from the L valleys, has been modified by the local potential and, for $x \gtrsim 0.22$, becomes the deep ground state.

THE DISPLACED DONOR MODEL

We now need to determine what kind of central cell potential could produce the large increase in T_2 binding energy observed. We conclude from the discussion above that it cannot come from a substitutional donor centered on a lattice site. We are given additional clues by the fact that the T_2 state, like every orbitally degenerate state, is subject to the Jahn-Teller (JT) effect,[27] and by the earlier observation that the deep bound state seems to be associated with a large lattice distortion.[2] This leads to the obvious suggestion that the depth of the T_2 state is driven by a JT displacement of the atoms of the central cell.[28]

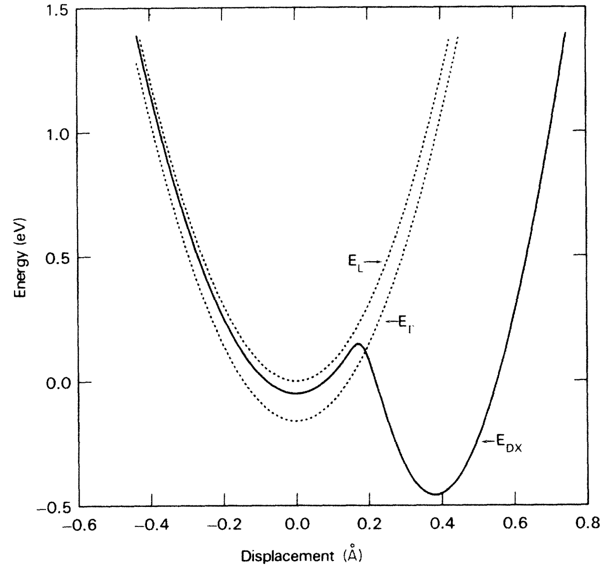

FIG. 2. A schematic diagram showing the dependence of the adiabatic energy levels of the DX center on donor displacement. The dotted lines show the L and Γ band edges and the solid the DX level. See the discussion in the text. The parameters have been chosen to give reasonable agreement with experiment.

To identify the important JT active lattice mode, we note that it must be degenerate (of symmetry E or T_2), must couple strongly to the highly localized state and, to minimize the elastic energy, must distort only the few bonds nearest the defect. The one mode which satisfies these criteria is the displacement, of symmetry T_2, of the central donor atom away from its symmetric position, most probably along a trigonal direction, accompanied by smaller adjustments of the neighboring atoms. The coupling is, thus, derived from the energy of the bond, which changes rapidly with interatomic separation, and the cost in elastic energy is approximately that associated with motion of a single atom.

The JT coupling between the displacement mode and the EM T_2 state bound to a centered donor is small because of the extended nature of the electronic wave function, and in the regime of small displacement this state acts as a normal degenerate state modified by a small JT effect.[29] Only when the local potential becomes strong enough to concentrate the electron probability in the nearest-neighbor bonds does the binding energy become large. This is shown schematically in Fig. 2 for a T_2 EM state (binding energy 50 meV) modified by a very local potential. The figure has used the one-band, one-site potential of Koster and Slater, which generates a bound state only if the potential exceeds a critical value.[30] Note that the short range-potential arises almost entirely from the distortion and is very small for the centered configuration. Hence, although the relaxed state is deep, the states at small and intermediate distortion are not, and, as is shown in the figure, there may be a maximum in total energy between two configurations, one stable and one metastable.[31] This potential barrier, which must be surmounted by either thermal activation or tunneling for capture or ionization to occur,[32] accounts for the very small low temperature capture rate (and, hence, PPC) and most clearly distinguishes *DX* centers from the majority of other deep centers. For these other centers the binding energy varies more gradually with lattice distortion, so that a potential barrier does not occur, and the capture rates are much larger.[33]

For the deep state to be stable, the sum of the Coulomb energy and the energy gained by displacement of the central atom must be large enough to overcome, not only the elastic energy of the lattice, but also the localization energy required to confine the electron to the neighborhood of the central cell. Estimates of these energies are easily made and agree with the ~1-eV thresholds observed in the photoionization experiments,[6] if these transitions go to the conduction band states in the region of high density near *L*.

The origin of the coupling energy may be visualized easily for a T_2 state formed from the four nearest-neighbor antibonding orbitals. The component of this state having a symmetry axis along one of the ⟨111⟩ directions has 75% of the electron probability density in that one orbital and only 25% in all of the other three. Consequently, displacing the central atom along ⟨111⟩ by an amount which lowers the energy of that orbital by Δ (and raises the energy of each of the other three by $\Delta/3$) lowers the total energy of the state by $2\Delta/3$. This suggests that in the relaxed deep state the donor will be displaced from its centered position away from one neighbor toward a position in the plane of the other three.

One cannot, of course, rely on a small displacement model to predict energy changes of the order of one electron volt, and a restructuring of the bonds which gives the minimum energy must be sought within the framework of the model. In the limit of a large displacement the electron wave function will be concentrated in the one orbital parallel to the displacement (which has the lowest energy), thus adding one antibonding to the two bonding electrons in this orbital and effectively canceling much of the bonding force.

A simple qualitative tight binding analysis, depicted in Fig. 3, yields useful insight about the energies of the deep donor states. The energies of the (filled) valence bands are not altered greatly by displacement of the donor—some bonds lengthen while others shorten—and their energies conform approximately to the crystal average (plus the elastic energy). As shown in Fig. 3, however, the energy (and wave function) of the relaxed *antibonding* states is determined mainly by the atomic orbitals on the group-III site, while the group-V levels dominate the *bonding* orbitals. Hence, the properties of the bound states will be different only if those wave functions on group-III sites are different.

This simple observation explains the chemical trends in the experimental energies—see Ref. 7 and Table I of Ref. 3. Although the binding energies of the deep states (for $x=0.4$) are found to be nearly independent of donor species,[6] the thermal activation energies for ionization or capture are not and are consistent with the arguments presented above:

(1) The activation energies of the group-IV donors (on group-III sites) depend on the donor species, being large for Si but small for Sn.

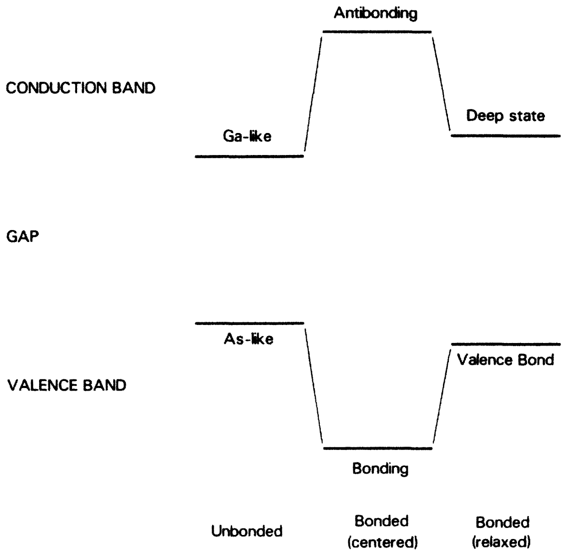

FIG. 3. A simplified tight-binding energy level diagram for the deep T_2 donor state in GaAs. Group-IV donors replace the Ga-like orbitals, group-VI donors the As-like orbitals. The figure shows schematically a progression from unbonded to bonded atomic orbitals and then to the relaxed configuration with the donor displaced parallel to the bond shown. The deep state is derived from antibonding orbitals on the Ga site. Note: the energy shift shown for the valence bond is largely compensated by other occupied bonds not included in the figure.

(2) The group-VI donors (on group-V sites) all have about equal (intermediate) activation energies, which are determined by that group-III atom having the lower energy, presumably Ga which lies deeper than Al.[34]

(3) Differences are also expected among group-VI donors according to the numbers of Al and Ga atoms they have as nearest neighbors.

(4) All substitutional donors are expected to exhibit the *DX* phenomena. The so-called "residual donors" which do not, and which are observed in the 10^{16} cm^{-3} concentration range[4] are, therefore, presumed to be *not substitutional,* but either interstitial donors or complexes.

(5) The binding energy depends on the (three) shortened bonds and is found to be nearly independent of donor species, cf. Table I of Ref. 3. This is because in the deep state both the bonding and antibonding orbitals of the lengthened bond are occupied, and the stable position (and energy) are determined by the remaining bonds.

The triplet nature of the deep states has additional consequences which must be considered in interpreting the data. In contrast to singlet states, which shift only quadratically with small strains, these states shift linearly with strains and with other electronic inhomogeneities in the alloys which lift their degeneracies. Thus, that component which is depressed in energy and, therefore, occupied at low temperature, determines the observed energy of the state and the temperature dependence of such phenomena as the Hall effect and thermal ionization. This explains the gradual change in relative occupancy of the shallow and deep levels with changing x as the Fermi level moves through the distribution of deep states (cf. Ref. 5 and Fig. 18 and Sec. 4.2 of Ref. 3). (It has also contributed to the confusion over identification of "normal" and deep donors.) The absence of these effects in compressed GaAs modifies the apparent binding energy of the deep state and probably accounts for the energy shifts relative to $Al_xGa_{1-x}As$ reported by Mizuta *et al.*[9] The displaced donor model, thus, provides an explanation of the major properties of DX centers.[35,36]

(1) The energies of the deep donor levels are roughly accounted for, including their chemical shifts.

(2) The model incorporates a large lattice relaxation, so that the analysis of Ref. 4, when modified to eliminate the in-band resonant state at small distortion, generally applies.

(3) The model accounts naturally for the potential barrier needed to explain the small capture rates and PPC.

(4) The model invokes an orbitally degenerate state, which provides a *natural* explanation of the lattice relaxation (through a JT effect) and explains the sensitivity to inhomogeneities and the resulting broadening and shift of the energy levels.

(5) The model explains the phonon attenuation data of Ref. 29, including the symmetries observed for the shallow states.

Several extensions of the work, however, are obviously needed:

(1) Quantitative calculations should be made to confirm that the potential associated with the displaced donor atom is strong enough to produce the deep T_2 state, as in Ref. 35.

(2) A careful analysis of the potential surfaces and of the transition rates between states of the displaced and centered configurations should be made in order to clarify the nature of these processes.

(3) Comparisons with experiment must be made to determine the relevant parameters of the model. In these it is important to keep in mind the experimental problems associated with the long lifetimes of the states, as noted above.[20]

(4) Because of the sensitivity of the triplet state energies to the strains and inhomogeneities in the alloys, many of the data should be reinterpreted.

(5) Experiments which test the symmetry of the deep state should be undertaken.[37] To avoid the random fields of the alloys, these should, if possible, be performed in GaAs under pressure.

ACKNOWLEDGMENTS

It is a pleasure to acknowledge numerous fruitful discussions with many colleagues, especially Walter Harrison, Milan Jaros, Pat Mooney, Socrates Pantelides, Tom Theis, Wen Wang, and Don Wolford. This work has been supported, in part, by the Office of Naval Research under Contract Nos. N00014-80-C-0376 and N00014-85-C-0868.

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[1] R. J. Nelson, Appl. Phys. Lett. **31**, 351 (1977).

[2] D. V. Lang and R. A. Logan, Phys. Rev. Lett. **39**, 635 (1977).

[3] See, also, the review by D. Lang, in *Deep Centers in Semiconductors,* edited by S. T. Pantelides (Gordon and Breach, New York, in press).

[4] D. V. Lang, R. A. Logan, and M. Jaros, Phys. Rev. B **19**, 1015 (1979).

[5] E. F. Schubert and K. Ploog, Phys. Rev. B **30**, 7021 (1984).

[6] D. V. Lang and R. A. Logan, in *Proceedings of the 14th International Conference of the Physics of Semiconductors, Edinburgh, 1978,* edited by B. L. H. Wilson, (IOP, Bristol, 1978), p. 433.

[7] O. Kumagai, H. Kawai, Y. Mori, and K. Kaneko, Appl. Phys. Lett. **45**, 1322 (1984).

[8] M. Tachikawa, T. Fujisawa, H. Kukimoto, A. Shibata, G. Oomi, and S. Minomura, Jpn. J. Appl. Phys. **24**, L893 (1985).

[9] M. Mizuta, M. Tachikawa, H. Kukimoto, and S. Minomura, Jpn. J. Appl. Phys. **24**, L143 (1985). These workers found the peaks shifted relative to those in the alloys—presumably because of the absence of inhomogeneous strain effects.

[10] This does not imply that only these states are active. Two others which have been observed optically are the shallow $2p$ state derived from the Γ minimum, discussed below, and an excited state in the relaxed configuration, see J. C. M. Henning, J. P. M. Ansems, and A. G. M. de Nijs, J. Phys. C **17**, L915 (1984).

[11] Estimates of the EM energies are easily obtained. The low-frequency dielectric constant ϵ_0 varies from 12.5 in GaAs to 10 in AlAs (Ref. 12), so that the $1s$ EM binding energy for effective mass m^* is $E_B=(m^*/m_0\epsilon_0^2)$ Ry or near $E_B\approx 100(m^*/m_0)$ meV. The masses may be estimated from the density-of-states masses for $x\approx 0.5$ from Ref. 13. Thus, $m_\Gamma^*\approx 0.1m_0$, $m_x^*\approx 0.4m_0$ (assuming three valleys) and $m_L^*\approx 0.25m_0$ (assuming four valleys), and the EM binding energies are $E_B\approx 10$, 40, and 25 meV, respectively.

[12] R. K. Watts, *Point Defect in Crystals* (Wiley, New York, 1977), p. 208, Table 8.1.

[13] H. C. Casey, Jr. and M. B. Panish, *Heterostructure Lasers* (Academic, New York, 1978), Part A, Table 4.2-1, p. 192.

[14] A. Pinczuk, Steven G. Louie, B. Welber, J. C. Tsang, and J. A. Bradley, Inst. Phys. Conf. Ser. No 43, 1979, *Proceedings of the 14th International Conference of the Physics of Semiconductors, Edinburgh, 1978* (Ref. 6), p. 1191. The conclusions of this work should be modified for the effects of the deep DX centers now known to be present in n-type GaAs.

[15] Exceptions might occur for impurities with a complex core—such as transition metal defects.

[16] T. N. Morgan, Phys. Rev. Lett. **21**, 819 (1968).

[17] The fact that groups-IV and -VI donors have very similar DX properties in spite of these symmetry differences is further evidence that the wave functions of the deep states have only small contributions from the X valleys.

[18] See Refs. 5 and 6, among many others.

[19] T. N. Theis, T. F. Kuech, L. F. Palmateer and P. M. Mooney, Inst. Phys. Conf. Ser. No. 74, *Proceedings of the 11th International Symposium on GaAs and Related Compounds, Biarritz, 1984,* edited by B. de Cremoux (IOP, Bristol, 1984), p. 241.

[20] Because of this isolation between the two types of states, as was noted in Ref. 1, it is extremely difficult to measure equilibrium concentrations, and many of the low-temperature published data are suspect.

[21] R. Dingle, R. A. Logan, and J. R. Arthur, *GaAs and Related Compounds, Edinburgh, 1976,* edited by C. Hilsum (IOP, Bristol, 1977), p. 210.

[22] N. Chand, T. Henderson, J. Klem, W. T. Masselink, R. Fischer, Y.-C. Chang, and H. Morkoç, Phys. Rev. B **30**, 4481 (1984).

[23] There is the possibility of an anticrossing near $x=0.2$ where the deep state and the $2p$ shallow excited state cross, although this should be very weak and narrow because of the small overlap between the shallow $2p$ state and the deep ground state (probably 0.01% of the A_1 matrix element) and because of the large lattice relaxation.

[24] The band edges shown in Fig. 1 have been taken from the review by Casey and Panish (Ref. 13). They are based largely on Fig. 2 of Dingle, Logan, and Arthur (Ref. 21). The L- and X-band energies deduced by other workers, for example, Saxena (Ref. 25), differ but do not materially alter the fit to the FIR data.

[25] A. K. Saxena, Phys. Status Solidi B **105**, 777 (1981).

[26] Note that the tight binding theory of impurities, which predicts that there will be one A_1 and one T_2 antibonding state either in the gap or resonant with the conduction band, leads to the same conclusion. See H. P. Hjalmarson, P. Vogl, D. J. Wolford, and J. D. Dow, Phys. Rev. Lett. **44**, 810 (1980).

[27] The JT theorem states that for every orbitally degenerate electronic state in a crystal there is at least one (degenerate) mode of lattice distortion which will distort spontaneously and lower the total (vibronic) energy of the coupled system. In the present example one $\langle 111 \rangle$ component of the triplet T_2 electron state has its energy lowered by a trigonal (T_2) displacement of the donor away from its symmetric lattice site. There are four such distorted states, although not all are independent. See R. Englman, *The Jahn-Teller Effect in Molecules and Crystals* (Wiley, New York, 1972), especially Chap. 3.

[28] A different way of viewing the distortion is suggested by the work of R. P. Messmer and P. A. Schultz, Solid State Commun. **52**, 563 (1984). Using a correlated valence bond theory to analyze off-center impurities in silicon, they find that the stable configuration of many impurities is off center. Although, because of their large displacements, such states are not strictly JT states, they have the same degeneracies and are qualitatively similar in many ways.

[29] This weak JT effect explains the anisotropic phonon attenuation reported by V. Narayanamurti, R. A. Logan, and M. A. Chin, Phys. Rev. Lett. **43**, 1536 (1979). Such attenuation is not expected when the deep states are occupied, because of the extremely long reorientation times of the distorted defects (related to the PPC relaxation times), and, indeed, it was observed only when the *DX* centers had been emptied by light. Also, the symmetries observed are consistent with the trigonal distortion expected for Sn, which bonds to four equivalent As atoms. The more complicated ("orthorhombic") symmetry found for Te, however, suggests that two adjacent bonds are lengthened to produce a $\langle 100 \rangle$ tetragonal distortion, which is further perturbed by a random distribution of nearest-neighbor Ga and Al atoms.

[30] G. F. Koster and J. C. Slater, Phys. Rev. **96**, 1208 (1954).

[31] This is analogous to the phenomenon of self-trapping of free carriers discussed by Y. Toyozawa, Solid State Electron. **21**, 1313 (1978). It corresponds to the region in which trapped carriers are stable, free carriers are metastable, and the two are separated by a potential barrier.

[32] Because of the complexity of the transition between the two configurations, the relaxation might better be thought of as a rebonding (Ref. 28), rather than as a Jahn-Teller effect (Ref. 27). In the relaxed configuration for a trigonal distortion (symmetry group C_{3v}) the symmetry of the deep electronic state is A_1, and there are four such equivalent states. Although these states are coupled, the mixing among them is, for large distortions, negligibly small. For this reason the effects of random strains in the crystals are also most important when the distortion is small. As a result, strains are more effective in modifying the barrier height than the depth of the state.

[33] It is misleading that a potential barrier due to band crossing is drawn in almost all C-C diagrams (see, for example, the diagrams in Ref. 4), although such an occurrence is an assumption which requires justification. Only in very unusual cases will the true adiabatic energy levels cross *related* band edges and produce in-band resonances. See the discussion of capture by T. N. Morgan, Phys. Rev. B **28**, 7141 (1983).

[34] A. Baldereschi, E. Hess, K. Maschke, H. Neuman, K.-R. Schulze, and K. Unger, J. Phys. C **10**, 4709 (1977).

[35] A model involving displacement of the four neighboring As atoms around a Si donor has been proposed by Atsushi Oshiyama and Shuhei Ohnishi, Phys. Rev. B **33**, 4320 (1986). In support of this model they present a cluster calculation showing that a tetragonal distortion (transforming as one component of the E representation in the T_d group) could lower the A_1 antibonding state into the forbidden gap. An inconsistency in the symmetry of the states and distortions involved raises some questions about the meaning of this result, and the large volume of the distortion proposed makes the stability of such a system seem less probable than that proposed in the present work.

[36] A somewhat similar model, in which the donor is displaced by differential coupling to surrounding Ga and Al atoms, has been proposed recently by K. L. I. Kobayashi, Y. Uchida, and H. Nakashima, Jpn. J. Appl. Phys. **24**, L928 (1985). Although the alloy effects considered might apply to group-VI (Te) donors, they seem inappropriate for Si (group IV). It is significant that these authors have reached a conclusion similar to that of the present work. The term "self-generated donor-vacancy pairs," however, which they introduce, suggests a major difference from the displaced-donor model in which no bonds are broken and the atomic displacements generate predominantly a lowering of the antibonding state.

[37] Such an experiment has been reported recently by F. Sette. S. J. Pearton, J. M. Poate, J. E. Rowe, and J. Stöhr., Phys. Rev. Lett. **56**, 2637 (1986), who performed an EXAFS study of GaAs so heavily doped with S ($n=2\times10^{19}$ and $2\times10^{20}\ \mathrm{cm}^{-3}$) that most of the donors were in their neutral *DX* state. They found that the Ga nearest neighbors occupied positions at two different distances from the S donors, as predicted by the displaced-donor model.