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Identification of the defect state associated with a gallium vacancy in GaAs and $Al_xGa_{1-x}As$

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Arguments based on new data as well as an analysis of the literature are given to show that the so-called $E3$ radiation-damage defect state in GaAs and $Al_xGa_{1-x}As$ is most likely a gallium vacancy. It is first shown that on the basis of chemical trends one should expect vacancies in GaAs to be stable at room temperature. It is then argued that most of the defects observed in room-temperature 1-MeV electron-irradiated GaAs are likely to be simply native defects rather than clusters or impurity complexes. Data on the orientation dependence of the defect production rate are given which show that the defects which recover at 500 K in GaAs are all due to Ga atom displacements. Finally, data are presented on the energy-level shifts of seven deep levels, including the $E3$ level, in $Al_xGa_{1-x}As$ as a function of Al mole fraction. These data show that the $E3$ level is anomalous and remains fixed relative to the valence band whereas all other levels shift in energy to maintain their same relative position in the gap. This anomalous behavior is interpreted on the basis of theories of surface dangling bonds and vacancy states to be evidence that the $E3$ level is a gallium vacancy.

I. INTRODUCTION

Isolated lattice vacancies have been observed in a number of semiconducting and ionic materials but not in III-V compounds. The best method for positively identifying such vacancies has been electron-paramagnetic resonance[1] (EPR). Watkins[2] points out that EPR identification of vacancies has been made in alkali halides (the familiar F centers), in the II-VI materials ZnS, ZnSe, ZnO, CdS, and BeO, and in silicon. In addition, according to Corbett and Bourgoin,[3] motion of the vacancy in germanium has been indirectly observed by EPR. One might ask why there is no similar EPR information about vacancies in III-V compounds. Apparently, the principal reason is that the hyperfine broadening due to the nuclei in groups III and V of the Periodic Table is at least an order of magnitude larger than for nuclei in groups II, IV, or VI. This follows from the fact that nuclei with both an even number of neutrons and protons have zero magnetic moment. Large nuclear-magnetic moments, and hence large hyperfine broadenings, are common among alkali halides, however. In spite of this, there is considerable information about lattice vacancies in these materials. The electron-nuclear double-resonance technique has been useful in such situations with unresolved hyperfine structure.[1] There appears to be no *intrinsic* reason why EPR cannot provide similar information about III-V native defects, albeit with some difficulty.

There have been many claimed identifications of native defects in III-V compounds in the literature. In particular, there has been considerable work on the effects of 700–1100 °C heat treatment on the optical and electrical properties of GaAs. Chiang and Pearson[4] show that much of the previous work in this area is dominated by impurity effects. They observe acceptors and donors diffusing into GaAs at 700–1000 °C and associate these with gallium and arsenic vacancies, respectively, on the basis of variations in concentration with arsenic overpressure during heat treatment. The energy levels of these nonradiative centers are not known, nor is it known whether they are isolated vacancies or complexes of vacancies and impurities. Also, the possibility that the defects are interstitials or antisite defects cannot be ruled out. Indeed, Driscoll, Willoughby, and Williams[5] have shown that the primary defects in nonstoichiometric arsenic-rich GaAs are either arsenic interstitials or arsenic atoms on gallium sites. Similarly, Kaufmann, Schneider, and Rauber[6] have recently observed by EPR in GaP grown by the liquid-encapsulated Czochralski method the antisite defect P_{Ga}, a phosphorus atom on a gallium site. Van Vechten[7] has suggested on theoretical grounds that antisite defects ought to be common nonstoichiometric defects in zinc-blende compounds. Thus admitting the possibility of interstitial and antisite defects, in addition to vacancies, we see that stoichiometric arguments can only distinguish between a gallium vacancy V_{Ga}, an arsenic interstitial As_i, or an arsenic antisite defect As_{Ga}, on the one hand, which are *all* enhanced by increased As overpressure and an arsenic vacancy V_{As}, a gallium interstitial Ga_i, or a gallium antisite defect Ga_{As}, on the other hand, which are decreased by increased As overpressure.

In the absence of EPR data it is very difficult to identify an isolated native defect in GaAs. No single experiment taken alone has the identification power of EPR. We believe, however, that a strong case can be made for the identification of the gallium vacancy in GaAs and $Al_xGa_{1-x}As$. The evidence is largely piecemeal and circumstantial in nature, but we believe convincing when viewed as a whole. In the remainder of the paper we will give our experimental results and outline the case for this identification.

In Sec. II we show on the basis of chemical trends in the literature that some isolated native defects in GaAs should be expected to be stable at room temperature. Section III is a discussion of the experimental methods used in this work. In Sec. IV experimental results are given which show that the defect in question is created by a gallium atom displacement. Finally, in Sec. V we show experimentally that the defect wave function is made up primarily of valence-band states and thus is most likely a vacancy.

II. CHEMICAL TRENDS IN DEFECT STABILITY

On the basis of a review of radiation damage literature it is possible to conclude that the radiation induced defects which are stable at room temperature in GaAs are most likely simple native defects — vacancies, interstitials, or antisite defects. Such a conclusion comes as something of a surprise if one is familiar primarily with Si and Ge or the two earliest studied III-V compounds, GaSb and InSb. The primary defects in these materials are all mobile and hence unstable below about 200 K.[3,8]

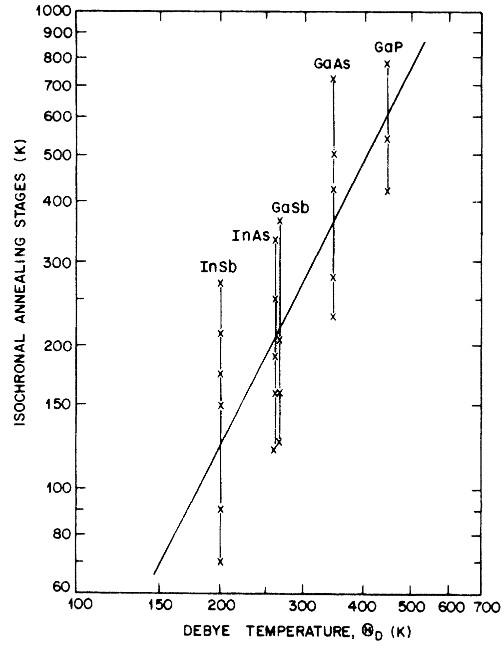

FIG. 1. Isochronal recovery stages in InSb, InAs, GaSb, GaAs, and GaP as a function of Debye temperature Θ_D. The line through the data shows a Θ_D^2 dependence.

Let us first consider the defect stability trends within the III-V group itself. In Fig. 1 we show the reported isochronal recovery stages versus Debye temperature[9] for InSb,[8] InAs,[10,11] GaSb,[12] GaAs,[13,14] and GaP.[15] The line drawn through the data is proportional to Θ_D^2. The reason for this Θ_D^2 dependence is not clear, but it is reasonable that the temperature of defect mobility should be correlated with the Debye temperature. This is because Θ_D is a measure of the temperature at which anharmonic effects in the lattice-vibration spectrum become important. Defect motion is clearly an anharmonic effect.

Isochronal recovery data such as shown in Fig. 1 are often difficult to interpret in terms of specific defects. It is generally accepted,[3,16] however, that for a given material the lowest-temperature stages are associated with simple defects while the higher-temperature stages are associated with defect clusters or impurity complexes. Thus from Fig. 1 we see that simple defects ought to be stable near room temperature in GaAs and well above room temperature in GaP.

Van Vechten[17] has proposed a simple ballistic model for vacancy migration which is remarkably successful in fitting the trends in vacancy migration enthalpy for 16 elemental crystals, mostly metals. In this model the enthalpy of vacancy motion is taken to be proportional to $\frac{1}{2}Mv^2$, where M is the mass of the nearest-neighbor atom jumping into the vacancy and v is the velocity needed to traverse a nearest-neighbor distance in a single lattice-vibration period. Thus, $v = d/\tau$ where d is the distance an atom must jump and $\tau = h/k\Theta_D$ is the lattice-vibration period in the Debye approximation. The enthalpy of vacancy motion is then proportional to $M(d\Theta_D)^2$. This is suggestive of the Θ_D^2 dependence of the defect motion in III-V compounds shown in Fig. 1. However, the large mass variation from InSb to GaP would tend to predict a much weaker dependence on Θ_D than is actually observed. Also, as Van Vechten points out, this simple model greatly overestimates the enthalpies of low-temperature motion for irradiation-produced vacancies in Ge and Si, the only covalent elemental crystals for which such data are available.

Nonetheless, it is of interest to consider the applicability of the $M(d\Theta_D)^2$ scaling law among the closely related semiconductors in the isoelectronic series Ge, GaAs, ZnSe. These three materials all have very similar lattice constants, crystal structures, masses, and Debye temperatures.[18] The principal difference, of course, is that Ge is an elemental crystal while GaAs and ZnSe are binary compounds. One would expect vacancy motion to be much easier in an elemental crystal than in a compound simply because the jump of a first nearest neighbor is needed for an elemental material whereas the jump of a *second* nearest neighbor is needed for a compound. A large difference in stability is in fact observed for vacancies in Ge as compared to ZnSe. The vacancy in Ge moves at approximately 120 K[3] while the zinc vacancy (V_{Zn}) in ZnSe becomes mobile at approximately 400 K.[19] Such a variation in recovery temperature roughly follows the $M(d\Theta_D)^2$ scaling law for these two materials. Since M and Θ_D are nearly the same for Ge and ZnSe, we must only consider the difference between a nearest-neighbor jump of $\frac{1}{4}\sqrt{3}\,a$ in the $\langle 111\rangle$ direction, and a second nearest-neighbor jump of $a/\sqrt{2}$ in the $\langle 110\rangle$ direction, where a is the unit cell dimension which is the same in both Ge and ZnSe. The square of the ratio of these distances is 2.67 while the ratio of the recovery temperatures is 3.3, quite reasonable agreement in view of the simplicity of the model. Thus, on the basis of comparison with Ge and ZnSe it is not at all unreasonable to expect to find stable isolated vacancies at room temperature in GaAs.

We can gain further insight into the probable behavior of vacancies in GaAs by considering trends due to variations in ionicity in the series: GaAs, ZnSe, KBr. One expects intuitively that native defects should move more easily in more ionic compounds, since the bond bending forces become smaller with increasing ionicity. Indeed, this is true when one compares KBr and ZnSe. *F* centers (V_{Br}) in KBr recover at about 150 K,[20] compared with V_{Zn} in ZnSe at 400 K. Similarly, interstitials move at 10–20 K in KBr,[20] compared with 60–180 K in ZnSe.[21] In addition, Phillips[22] has shown that the cohesive energy of tetrahedrally bonded crystals in the same row of the Periodic Table decreases linearly with ionicity, e.g., Ge, GaAs, ZnSe. For such a series with similar lattice constants and mass, the cohesive energy is proportional to bond energy. If we assume that similar bonds are broken in the migration path of both V_{Zn} and V_{Ga} in ZnSe and GaAs, respectively, then the defect recovery temperature should scale as the cohesive energy. The cohesive energy of GaAs is 1.33 times that of ZnSe.[22] Thus if we scale the 400-K recovery temperature of V_{Zn} by a factor of 1.33 we might expect V_{Ga} to recover at 532 K. Indeed, as we will show, the center which we believe is the gallium vacancy in GaAs recovers at about 500 K. This is in remarkably good agreement with the chemical trends in the Ge, GaAs, ZnSe, KBr series and is a strong background for the following experimental results which give further independent support for the V_{Ga} identification.

III. EXPERIMENTAL TECHNIQUES

The experimental results to be presented in this paper are all obtained by the technique of deep-level transient spectroscopy (DLTS). This has been discussed adequately in previous papers[23] and will not be repeated in detail here. Suffice it to say that the technique is essentially a method of "nonradiative spectroscopy" whereby deep levels in the gap of a semiconductor may be displayed as a spectrum of positive and/or negative peaks as a function of temperature, which is roughly equivalent to an energy scale. The concentration of a deep level may be readily measured in addition to the activation enthalpy for thermal emission of a carrier to the nearest band edge. The various corrections necessary to obtain the final energy of the level have been discussed by Lang and Logan.[24]

The samples used in this study were in the form of p^+n junctions grown by liquid-phase epitaxy (LPE), heavily doped with Ge on the p^+ side ($\sim 10^{18}$ cm^{-3}) and either undoped or Sn doped on the n side [$(0.5\text{–}5.0)\times 10^{16}$ cm^{-3}]. Most GaAs and $\text{Al}_x\text{Ga}_{1-x}\text{As}$ samples were grown on (100) oriented n^+ substrates. For the orientation experiments p^+n junctions were also formed by layer growth on the (110), (111) Ga, and (111) As faces. The (111) Ga face was distinguished from the (111) As face by their different chemical-etching behaviors.[25] For these oriented samples the junction depth was always less than 6 μm from the surface so that loss of the 1-MeV electron beam orientation due to multiple scattering could be neglected. For the study of the deep-level shifts as a function of crystal composition in $\text{Al}_x\text{Ga}_{1-x}\text{As}$, a series of p^+n homojunctions with $0 \leqslant x < 0.35$ were grown. Some were undoped, others were intentionally doped with Cu or Fe.

The electron irradiations were performed at room temperature with a 1-MeV Van de Graaff accelerator. The beam flux was 6×10^{11} electrons cm^{-2} sec^{-1} (0.1 μA/cm^2). The total integrated flux (fluence) was typically $\Phi = 10^{15}$ cm^{-2}. For the orientation experiments four diodes grown on (100), (110), (111), and $(\bar{1}\bar{1}\bar{1})$ substrates were irradiated simultaneously.

IV. ORIENTATION EFFECTS

A. Other III-V compounds

Because of the polar nature of the zinc-blende crystal structure it is often possible to identify the sublattice responsible for a particular native defect by studying the orientation dependence of the defect production rate due to high-energy electrons. The anisotropy of damage for electrons incident on the (111) *A* and (111) *B* faces, respectively, of InSb and GaSb was used to associate the first recovery stage in these two materials with displacements of the group-V atoms and the second recovery stage with group-III displacements.[8] In addition, the group-III displacements in both cases were found to have lower-damage threshold energies.[8] This is very reasonable in view of a recent theory by Van Vechten,[26] who showed that the Frenkel pair-production threshold energy is dominated by the energy of the interstitial atom. This is given roughly by the product of the number of valence electrons of the atom times one-half the average dielectric band gap of the material. Thus for comparable atomic masses group-III atom displacements should in general be expected to have lower-damage thresholds than group-V atoms, as is found in InSb and GaSb.

On the basis of these considerations, Thommen[14] conjectured from carefully correlated recovery and damage threshold data that the 235- and 280-K recovery stages in GaAs were due to As displacements and the 500-K recovery stage was due to Ga displacements. As we will show, our orientation dependence measurements confirm this idea and show GaAs to behave in a manner consistent with the models for InSb and GaSb and with Van Vechten's theory.

B. GaAs defect spectra

Figure 2 shows the DLTS spectrum of LPE *n*-GaAs irradiated with 1-MeV electrons at room temperature. Two hole traps of unknown origin, labeled *A* and *B*, are nearly always present in the as-grown LPE material with concentration in the mid-10^{14}-cm^{-3} range. The radiation damage introduces six additional deep-defect states: five electron traps, *E*1, . . . , *E*5, and one hole trap, *H*1. The introduction rates, energy levels, and recovery rates in (100) oriented samples have been reported in earlier papers.[23, 27-29] All states except *E*4 recover at approximately 500 K in two groups. The levels (*E*3, *E*5, *H*1) recover together obeying first-order kinetics with an activation energy of 1.4 ± 0.15 eV and an exponential prefactor of $10^{12\pm1}$ sec^{-1}. The levels (*E*1, *E*2) recover together also with first-order kinetics and an activation energy of 1.75 ± 0.17 eV with a prefactor of $10^{13\pm1}$ sec^{-1}. These two groups correspond, respectively, to the λ_1 and λ_2 substages reported by Aukerman and Graft.[13]

We have measured the defect spectra in various samples and find that levels *E*4, *E*5, and *H*1 are most likely related to impurities or higher-order clusters since their introduction rates vary widely in different samples. The introduction of levels *E*1, *E*2, and *E*3, on the other hand, show no such fluctuations and hence we conclude these are native defects. Likewise, the trends observed in the DLTS spectra as the mass of the bombarding particle is increased also suggests that *E*1, *E*2, and *E*3 are *simple* defects.[16, 30] One finds in this case that the spectra for various GaAs samples irradiated with 1-MeV electrons, 400 keV protons, 1.8-MeV α-particles, and 185-keV O^+ ions show an increased concentration of *E*4-like defects along with considerable broadening and a marked decrease in the *E*1, *E*2, and *E*3 signals. Since heavy particle damage promotes creation of defect clusters at the expense of isolated defects, we believe that *E*1, *E*2, and *E*3 are isolated native defects.

The lack of impurity effects for the dominant levels present in electron-irradiated samples is also supported by the recent results of Kol'chenko and Lomako[31] who find no impurity effects over a wide range of dopants in room-temperature electron-irradiated GaAs. This is an important observation since a dependence of the damage rate on chemical dopants is usually evidence that the primary native defects are unstable with respect to the creation of impurity complexes. In both Si and Ge the vacancy recovery stage is well correlated with the appearance of vacancy-impurity complexes which then dominate the material properties.[3] Similarly, in ZnSe the onset of vacancy motion corresponds to the creation of the well-known donor-vacancy luminescence complex.[32] In GaAs im-

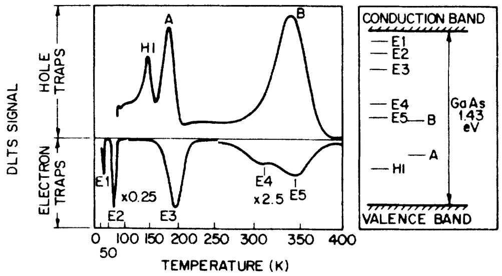

FIG. 2. DLTS spectrum of *n*-GaAs irradiated at room temperature with 1-MeV electrons. Levels *A* and *B* are present before irradiation. Irradiation-induced levels are the five electron traps *E*1, . . . , *E*5 and one hole trap *H*1. The relative positions of the levels in the gap are shown in the inset on the right-hand side of the figure. Note the compressed scale for *E*1 and *E*2 and the expanded scale for *E*4 and *E*5.

purity-defect luminescence complexes are observed to form during the 500-K recovery stage.[16] This is further evidence that the defects which recover in this 500-K stage are simple native defects.

C. Orientation dependence of defect production in GaAs

The results of the orientation experiment are given in Fig. 3. The beam orientations used are shown on the right-hand side of the figure in the (110) plane of the GaAs unit cell. Note the positions of the tetrahedral interstitial sites marked by dashed circles. We consider the simple model in which atoms are preferentially displaced in the forward-beam direction. In this model the probability of creating a V-i pair is enhanced when there is an empty interstitial site accessible to the recoiling nucleus in the forward-beam direction. The enhanced probability of V-i pair creation due to forward-recoil events into accessible interstitial sites has been demonstrated by Watkins[21] who observed by EPR a factor-of-3 asymmetry in the production rate of ⟨111⟩ V_{Zn}-Zn_i pairs aligned in the forward-beam direction in ZnSe irradiated with 1.5-MeV electrons along the ⟨111⟩ and $\langle\overline{111}\rangle$ directions, respectively. His model is exactly that of Fig. 3 with the displacement of the Zn atom being into the *second* interstitial site along the ⟨111⟩ direction when the beam is incident on the (111) Zn face of the crystal. As we discussed earlier, ZnSe is very similar to GaAs so that we expect the forward-displacement model to be valid here as well.

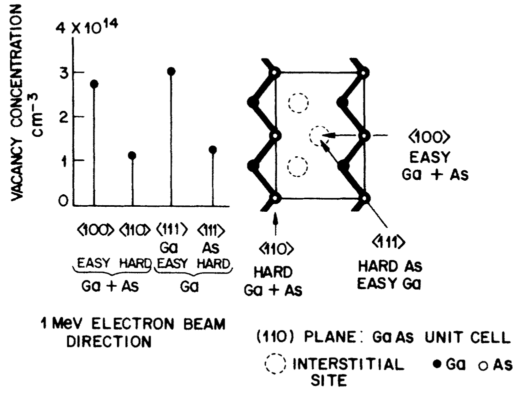

FIG. 3. Orientation dependence of the introduction rate of the $E3$ level (gallium vacancy). Four samples with (100), (110), (111) Ga, and (111) As surfaces exposed to the 1-MeV electron beam were irradiated simultaneously to a total fluence of $\Phi = 1 \times 10^{15}$ cm^{-2}. The right-hand side of the figure is the (110) plane of the GaAs unit cell and illustrates three of the four sample orientations used. The "easy" and "hard" notations are explained in the text.

Consider first the situation for the electron beam along the ⟨110⟩ and ⟨100⟩ directions. For the beam along the ⟨110⟩ direction an accessible interstitial position is not available in the forward-beam direction. We call this a "hard" damage direction. The ⟨100⟩ orientation is an "easy" damage direction, however. As seen in Fig. 3, this direction displaces an atom directly into an interstitial site. These simple concepts agree well with experiment as seen on the left-hand side of Fig. 3 which shows the concentration of the $E3$ center for the same 1-MeV electron fluence Φ in four different directions. Note that the defect production rate for the ⟨100⟩ direction ("easy" for Ga *and* As) is nearly three times larger than for the ⟨110⟩ direction ("hard" for Ga *and* As). This anisotropy does not identify to which sublattice the defects belong but it does suggest that the simple forward-displacement model for "easy" and "hard" damage directions is likely to be valid.

The sublattice identification is obtained from the anisotropy of damage along the ⟨111⟩ direction into the Ga face and the ⟨111⟩ direction into the As face. The right-hand side of Fig. 3 shows the ⟨111⟩ direction into the Ga face. According to the forward-displacement model, this orientation is "easy" for Ga displacement, with two interstitial positions directly behind the atom, but "hard" for As displacement, with a Ga atom blocking the path to these interstitial positions. The opposite is of course true for the ⟨111⟩ direction into the As face. Since these polar (111) faces can be readily identified by their different chemical-etching behavior we have a convenient way to differentiate between damage on the two sublattices. As shown in the graph on the left-hand side of Fig. 3, the same factor-of-3 anisotropy exists for the two ⟨111⟩ directions as for the ⟨110⟩ vs ⟨100⟩ directions. The largest damage rate is for the electron beam incident on the (111) Ga face, the "easy" Ga displacement orientation. Thus we conclude that the $E3$ defect is associated with the displacement of a Ga atom.

The same anisotropy is also observed for the $E1$ and $E2$ defects, indicating that they are also related to Ga displacement. The orientation dependence of the impurity related $E4$, $E5$, and $H1$ levels are harder to interpret, but the anisotropy of their production is also consistent with Ga site displacements. Thus we see that *all* of the defects introduced by room-temperature electron irradiation can be related to Ga site displacements. This is consistent with the fact that these defects (except $E4$) all recover at 500 K and have the same damage production threshold energy.[14] The higher threshold defects, which recover at 235 and 280

K,[14] are thus presumably As-related damage, although orientation experiments need to be done to confirm this assignment.

As a result of the evidence presented thus far we can conclude that the $E1$, $E2$, and $E3$ defects are either V_{Ga}, Ga_i, or an antisite defect. The V_{Ga} and Ga_i possibilities are straightforward conclusions based on Fig. 3. The antisite defects and the possibility of close Frenkel pairs need some further comment. First, we believe we can rule out Frenkel pairs because of the dependence of the 500-K recovery rate on donor concentration and the appearance of donor-defect complexes at this temperature.[16] Both of these argue for long-range motion of the defects involved and not close-pair recombination. Also, in ZnSe Frenkel pairs are observed to *break up* at 180 K leaving only isolated V_{Zn}.[21, 32] Apparently the relaxation around the vacancy inhibits the recombination of the V-i pair.

The problem of antisite defects is more difficult. It is not clear from Fig. 3 whether the orientation data would predict $\mathrm{As}_{\mathrm{Ga}}$ or $\mathrm{Ga}_{\mathrm{As}}$. Antisite defect creation is a complex process which depends on an interstitial moving to a vacancy of the opposite type, e.g., $\mathrm{As}_i + V_{\mathrm{Ga}} = \mathrm{As}_{\mathrm{Ga}}$. If we assume that As_i are mobile at 300 K, then $\mathrm{As}_{\mathrm{Ga}}$ depends on the concentration of V_{Ga}. Also, "knock-on" displacements into the (111) Ga face would create $\mathrm{As}_{\mathrm{Ga}}$. Thus we believe that the data suggest $\mathrm{As}_{\mathrm{Ga}}$ as the most likely antisite-defect possibility.

In this section we have shown that the $E1$, $E2$, and $E3$ defects are Ga site related and have given evidence that they are simple, isolated defects and not complexes or clusters. In Sec. V we will show that the $E3$ level is most likely a vacancy.

V. ENERGY-LEVEL SHIFTS IN $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{As}$

We have measured the shifts in the DLTS spectra of seven deep levels in $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{As}$ mixed crystals as a function of the Al mole fraction x. Four of the levels are deep-hole traps: two of these (A and B) are of unknown origins but are always present in LPE GaAs, the two others are the well-known deep levels due to Cu and Fe.[24] The other three levels are the irradiation-induced electron traps $E1$, $E2$, and $E3$. By measuring the activation energies of these levels in different samples as a function of x we obtain the data shown in Fig. 4. Here we have plotted the energy position of the various levels in the gap as a function of x. The zero of energy corresponds to the top of the valence band and the energies of the A, Cu, Fe, and B levels are simply their (corrected)[24] activation energies for hole emission. The positions of the $E1$ and $E2$ electron traps are obtained by subtracting their (corrected)[24] activation energies from the energy of the Γ conduction-band minimum of $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{As}$.[33]

The positioning of the $E3$ level is crucial to our argument and deserves special attention. As pointed out in Ref. 28 there is a substantial (0.1-eV) correction in the energy of $E3$ due to the temperature dependence of the electron-capture cross section.[24, 34] The temperature dependence of the capture cross section has been measured for $E3$ in $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{As}$. We find that the electron-capture cross section σ_n decreases with x and that the activation energy of this cross section increases to 0.14 eV at $x = 0.22$. These changes occur in such a way that the general shape of $\sigma_n(T)$ is consistent with the multiphonon nonradiative capture theory[34] for $0 \leq x \leq 0.22$ (the only range measured). The *uncorrected* activation energy of $E3$ would make the level in Fig. 4 actually *drop* in the gap, with increased x, whereas the corrected energy of $E3$ places the level at a constant energy (1.1 eV) from the valence band for $0 \leq x \leq 0.22$.

The relative energy shifts in Fig. 4 are easier to compare when plotted as the normalized energy shift $E(x)/E(0)$, in Fig. 5. The solid line in Fig. 5 is the normalized shift of the $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{As}$ direct band gap. Note that all levels except $E3$ have roughly the same relative shift as does the direct gap. (The present data do not extend into the indirect-gap region, $x \gtrsim 0.4$.) The $E3$ level is clearly anom-

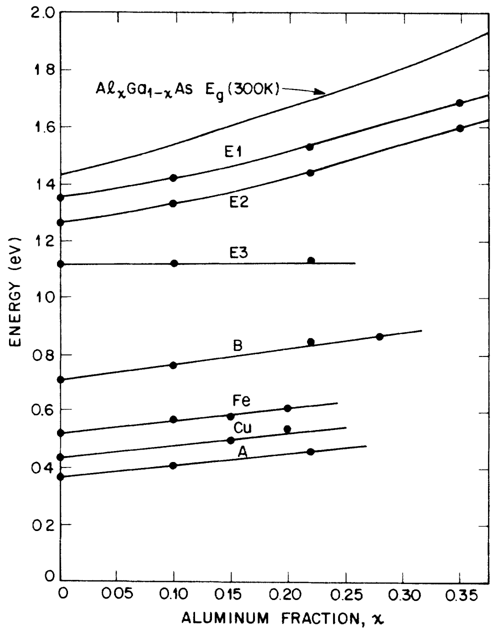

FIG. 4. Energy levels of seven deep levels in $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{As}$ as a function of Al mole fraction x. Levels $E1$, $E2$, and $E3$ are the irradiation-induced electron traps discussed in the text. Levels A and B are deep hole traps of unknown origin always present in LPE GaAs and Cu and Fe are the well-known deep levels associated with these impurities.

alous, however, and remains fixed to the valence band.

The data in Figs. 4 and 5 may be interpreted as follows: Most defects, i.e., impurities, bonded interstitials, and antisite defects, participate in the bonds of the crystal and have wave functions made up from both the conduction and valence bands. As the conduction band varies by increasing the Al mole fraction the admixture of conduction-band wave functions varies inversely with the energy separation from the conduction band and the energy of the deep level maintains its same *relative* position in the gap. That is to say, a level at midgap will sense one-half of the conduction-band change, a level near the valence band will change very little, and a level near the conduction band will be strongly influenced by changes in this band. The fact that six out of seven deep levels studied behave in this way is not surprising. What is surprising is a level such as $E3$ which is near the conduction band but is quite independent of changes in it. Apparently the $E3$ defect state is made up primarily of valence-band states.

The anomalous behavior of the $E3$ defect state indicates that it is substantially different from an impurity or antisite defect. A possible candidate for such a qualitatively different defect is a lattice vacancy, which in a tetrahedral semiconductor is an empty lattice site with four dangling bonds extending into it from the former first neighbors of the missing atom. These dangling bonds are quite analogous to the dangling bonds on a semiconductor surface. In silicon it is well known from theoretical treatments that the surface dangling bond states are valence-band-like in character.[35] Louie *et al.*[36] recently showed that the silicon vacancy is also made up of valence-band states, in agreement with the surface dangling-bond analogy. Thus we might expect on the basis of the silicon vacancy that the valence-band character of the $E3$ state is evidence that this state is also a vacancy.

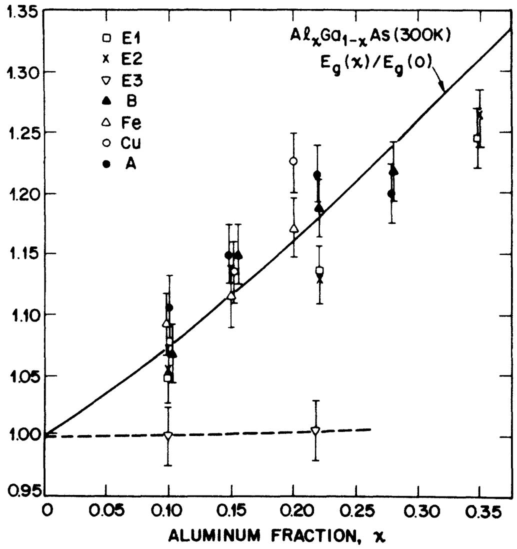

FIG. 5. Relative energy level shifts $E(x)/E(0)$ vs Al mole fraction x. This figure shows the same data as Fig. 4 plotted in a normalized fashion to exhibit the similarities in the behavior of all levels except $E3$.

The GaAs case is more complicated than Si, however, since we must consider the behavior of both As and Ga dangling bonds. Chelikowsky and Cohen[37] have shown that on the unreconstructed GaAs (110) surface the As dangling bonds are strongly valence-band-like in character while the Ga dangling bonds are associated with the conduction band. The relaxation which this surface undergoes during reconstruction, however, changes the character of the dangling bonds somewhat.[38] Hence, in analogy, we might expect the gallium vacancy (As dangling bonds) to be strongly valence-band-like in character, insensitive to lattice relaxation; whereas the character of the arsenic vacancy (Ga dangling bonds) should depend strongly on the amount of lattice distortion around the vacancy.[35] Jaros and Brand[39] have theoretically analyzed the gallium and arsenic vacancy states in GaAs and find *both* to be strongly hybridized with the valence band. They find that the V_{Ga} states are near the valence band and the V_{As} states are near the conduction band, which is similar to the location of the unreconstructed (110) As and Ga surface dangling-bond states, respectively.

Thus we see that strong valence-band-like character is a property of vacancies in GaAs as well as in Si. We propose on this basis that the $E3$ defect state is a vacancy. From the orientation measurements we can further say that it is a *gallium vacancy*. One might ask whether the theoretical treatments mentioned above could give some independent corroboration to the gallium identification obtained from the orientation experiments. We think not. As mentioned above, both the relaxed (110) surface and vacancy calculations predict predominantly valence-band-like character for both types of dangling bonds. On the basis of the energy levels obtained by Jaros and Brand, the $E3$ state energy is apparently like that of the arsenic vacancy level, i.e., near the conduction band in GaAs. The clear-cut results of the orientation dependence, however, show that this is not the correct identification. Apparently, relaxation effects, which may be larger than Jaros and Brand estimate, are important in determining the final energy of V_{Ga}.

We should stress, however, in connection with energy-level comparisons that the experimentally measured energy is *not* the energy of a single state of the vacancy but is actually the *difference* between the vacancy energy before emitting an electron and the energy of the vacancy with one less electron plus an electron in the conduction band. Because the vacancy energy is likely to depend strongly on its charge state due to electron-electron interactions, as it does in Si and as Jaros and Brand predict for GaAs, we cannot compare our electron thermal emission energy *difference* with the theoretical energy of only *one* of the vacancy charge states. For example, Jaros and Brand show that the gallium vacancy single-electron energy level drops by a few tenths of an electron volt when an electron is removed from the doubly occupied state. Thus the final-state energy of the system for a process involving the thermal or optical emission of this electron is *instantaneously* lowered by the amount of the electron-electron interaction energy. Consequently the apparent experimental energy for removing this electron is the depth of the two-electron state *minus* the interaction energy. That is to say, *the electron emission energy is lowered by the electron-electron repulsive energy*. This is to be contrasted with lattice-relaxation effects where the changes in an energy level after carrier emission or capture are not instantaneous but occur on the time scale of lattice-vibration frequencies. These lattice-relaxation effects are observable as Stokes shifts in the luminescence and absorption of the defect.

Finally we might mention that the independence of V_{Ga} from the conduction band makes sense on very simple atomic grounds. The changes in the conduction band of $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{As}$ come about when Ga atoms are replaced by Al atoms. The gallium vacancy is not strongly affected by this replacement, however, since the gallium (or aluminum) vacancy is always formed by four arsenic atoms in $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{As}$ for all x. On these grounds one might expect the arsenic vacancy to depend more strongly on alloy disorder. For example, even at a fixed value of x the V_{As} defect could be formed by four Ga, one Al and three Ga, two Al and two Ga, etc. Since deep defect states are quite localized we might expect local alloy disorder to have a larger effect on V_{As} than on the overall bandstructure, and certainly a larger effect on V_{As} than on V_{Ga}.

The strong coupling of $E3$ to the valence band, manifested in the lack of an energy shift with x in $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{As}$, is also evident in the carrier-capture cross section of this center. The electron-capture cross section of $E3$ in GaAs at 350 K is $\sigma_n = 5 \times 10^{-16}$ cm^2.[34] The hole-capture cross section, on the other hand, is $\sigma_p \sim 5 \times 10^{-15}$ cm^2, inferred from σ_n and the fact that $E3$ saturates with hole injection at approximately 1 A/cm^2.[27,28] The presence of such a large hole-capture cross section for a level 1.1 eV from the valence band implies very strong coupling to the valence band and considerable lattice relaxation. The situation is reminiscent of the very large hole-capture cross section observed for the two electron state of oxygen in GaP — a level which apparently is 1.3 eV from the valence band from thermal-emission measurements, but which actually relaxes very close to the valence band in a proper configuration coordinate picture.[34]

Finally, the fact that the $E3$ center exhibits strong recombination enhanced motion[27,28] due to hole capture is also evidence for its strong coupling to the valence band. This is evidence for very strong electron-lattice coupling associated with nonradiative hole capture on this defect.

We believe that given the choice among V_{Ga}, Ga_i, and $\mathrm{As}_{\mathrm{Ga}}$, the anomalous behavior of $E3$ presented in this section forces one to choose the gallium vacancy identification as clearly the most reasonable. It is hoped that EPR studies in the future will test this assignment — which, short of EPR, is probably about as firm an identification as one can make.

The identification of $E1$ and $E2$ is far less straightforward, however. Given a choice between only Ga_i or $\mathrm{As}_{\mathrm{Ga}}$ we might choose $\mathrm{As}_{\mathrm{Ga}}$ based on the energy-level shifts with x in $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{As}$ and on the fact that $E1$ and $E2$ are slightly *more* stable than $E3$ (V_{Ga}). One would expect Ga_i to be considerably less stable than V_{Ga} on the basis of results in Si, Ge, ZnSe, and the alkali halides where interstitials are much less stable than vacancies. Identifying $E1$ or $E2$ as Ga_i is also a problem in view of the fact that these levels are always about four times larger in concentration than is $E3$ (V_{Ga}). We cannot rule out the possibility that $E1$ and $E2$ are two levels of the same defect. The magnitudes of these signals are typically not equal (see Fig. 2) but this may be due to the incomplete filling of $E1$ during the majority carrier pulse used to generate the DLTS spectrum. Indeed, measurements of the $E1$ electron-capture rate indicate that it is very slow and may well be only partially filled under the conditions of Fig. 3.[29] The $\mathrm{As}_{\mathrm{Ga}}$ antisite defect should be a double donor and might naively be expected to have two levels near the conduction band, such as $E1$ and $E2$. We must emphasize, however, that this assignment is by no means as firmly based as our belief that the $E3$ center is a gallium vacancy.

VI. SUMMARY

In this paper we have tried to show in a series of interrelated arguments that the $E3$ radiation damage defect state in GaAs and $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{As}$ is most likely a gallium vacancy. We first showed on the basis of chemical trends in the literature that one should expect vacancies in GaAs to be stable above room temperature. We then showed that the main defects observed in room-temperature electron-irradiated GaAs are most likely simple defects and not clusters or impurity complexes. We presented data on the orientation dependence of the damage production rate to show that the defects which recover at 500 K in GaAs are due to Ga atom displacements. Finally, we showed on the basis of energy level shifts in $Al_xGa_{1-x}As$ as a function of x that the $E3$ level is fixed to the valence band while all other levels shift in the gap maintaining their same relative energy positions. We interpret this result to indicate that the $E3$ level is a vacancy. Considering all of this evidence as a whole we conclude that by far the most reasonable identification of the $E3$ defect state is a gallium vacancy.

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[1] G. D. Watkins, in *Point Defects in Solids*, Vol. 2, edited by J. H. Crawford, Jr. and L. M. Slifkin (Plenum, New York, 1975), p. 333.

[2] G. D. Watkins, in *Radiation Damage and Defects in Semiconductors* (Institute of Physics, London, 1973), p. 228.

[3] J. W. Corbett and J. C. Bourgoin, in Ref. 1, p. 1.

[4] S. Y. Chiang and G. L. Pearson, J. Appl. Phys. 46, 2986 (1975).

[5] C. M. H. Driscoll, A. F. W. Willoughby, and E. W. Williams, J. Mater. Sci. 9, 1615 (1974).

[6] V. Kaufmann, J. Schneider, and A. Räuber, Appl. Phys. Lett. 29, 312 (1976).

[7] J. A. Van Vechten, J. Electrochem. Soc. 122, 423 (1975).

[8] F. H. Eisen, in *Radiation Effects in Semiconductors*, edited by J. W. Corbett and G. D. Watkins (Gordon and Breach, New York, 1971), p. 273.

[9] V. Piesbergen, in *Semiconductors and Semimetals*, Vol. 2, edited by R. K. Willardson and A. C. Beer (Academic, New York, 1966), p. 49.

[10] R. Bauerlein, Z. Naturforsch. A 16, 1002 (1961).

[11] D. J. Lindsay and P. C. Banbury, in Ref. 2, p. 34.

[12] K. Thommen, Phys. Rev. 161, 769 (1967).

[13] L. W. Aukerman and R. D. Graft, Phys. Rev. 127, 1576 (1962).

[14] K. Thommen, Radiat. Eff. 2, 201 (1970).

[15] E. Yu. Brailovskii, I. D. Konozenko, and V. P. Tartachnik, Fiz. Tekh. Poluprovodn. 9, 769 (1975) [Sov. Phys. Semicond. 9, 505 (1975)].

[16] D. V. Lang, Proceedings of the International Conference on Radiation Effects in Semiconductors, Dubrovnik, 1976 (Institute of Physics, London, to be published).

[17] J. A. Van Vechten, Phys. Rev. B 12, 1247 (1975).

[18] S. I. Novikova, in Ref. 9, p. 40.

[19] G. D. Watkins, in Ref. 8, p. 301.

[20] E. Sonder and W. A. Sibley, in Ref. 1, Vol. 1, p. 201.

[21] G. D. Watkins, in *Lattice Defects in Semiconductors, 1974* (Institute of Physics, London, 1975), p. 338.

[22] J. C. Phillips, *Bonds and Bands in Semiconductors* (Academic, New York, 1973), p. 48.

[23] D. V. Lang, J. Appl. Phys. 45, 3023 (1974); D. V. Lang and L. C. Kimerling, in Ref. 21, p. 581.

[24] D. V. Lang and R. A. Logan, J. Electron. Mat. 4, 1053 (1975).

[25] H. C. Gatos and M. C. Lavine, J. Electrochem. Soc. 107, 427 (1960).

[26] J. A. Van Vechten, in Ref. 16.

[27] D. V. Lang and L. C. Kimerling, Phys. Rev. Lett. 33, 489 (1974).

[28] L. C. Kimerling and D. V. Lang, in Ref. 21, p. 589.

[29] D. V. Lang, L. C. Kimerling, and S. Y. Leung, J. Appl. Phys. 47, 3587 (1976).

[30] L. C. Kimerling, D. V. Lang, R. A. Logan, and W. M. Gibson (unpublished).

[31] T. I. Kol'chenko and V. M. Lomako, Fiz. Tekh. Poluprovodn. 9, 1757 (1975) [Sov. Phys. Semicond. 9, 1153 (1975)].

[32] G. D. Watkins, in Ref. 16.

[33] M. B. Panish, IEEE Trans. Microwave Theory Technique MTT-23, 20 (1975).

[34] D. V. Lang and C. H. Henry, Phys. Rev. Lett. 35, 1525 (1975); C. H. Henry and D. V. Lang, Phys. Rev. B 15, 989 (1977).

[35] M. Schluter (private communication).

[36] S. G. Louie, M. Schluter, J. R. Chelikowsky, and M. L. Cohen, Phys. Rev. B 13, 1654 (1976).

[37] J. R. Chelikowsky and M. L. Cohen, Phys. Rev. B 13, 826 (1976).

[38] J. R. Chelikowsky, S. G. Louie, and M. L. Cohen, Phys. Rev. B 14, 4724 (1976).

[39] M. Jaros and S. Brand, Phys. Rev. B 14, 4494 (1976).