PHYSICAL REVIEW B VOLUME 32, NUMBER 8 15 OCTOBER 1985

Atomic model for the M center in InP

J. F. Wager
Department of Electrical and Computer Engineering, Oregon State University, Corvallis, Oregon 97331

J. A. Van Vechten
IBM Thomas J. Watson Research Center, P.O. Box 218, Yorktown Heights, New York 10598
(Received 26 March 1985)

As described by Levinson *et al.*, the metastable M center in electron-irradiated InP is a complex of at least two point defects that exists in two very distinct atomic configurations, one of which has two variants, and that transforms from one configuration to another with a "large lattice relaxation" at low temperatures. When the Fermi level is not too close to either band edge, the complex is net neutral in one configuration and ionized triply positive in the other. We propose a simple atomic model for this center which identifies the neutral configuration as a second-nearest-neighbor antisite-vacancy pair $(V_{In}{}^{-}\text{-}P_{In}{}^{+})^0$, and the triply ionized configuration as $P_{In}{}^{+}\,V_P{}^{+}\,P_{In}{}^{+}$. We identify the "large lattice relaxation" as nearest-neighbor hopping of an In vacancy, which was created by the irradiation.

I. INTRODUCTION

The phenomenon that is commonly called "large lattice relaxation"[1,2] is a complexity widely observed in III-V compound semiconductors involving the behavior of those point defects that have more than one ionization state. It amounts to a change in position of all other ionization levels that occurs when a particular level is occupied or emptied. By analogy with the Franck-Condon shift in molecules, this is commonly attributed to a change in the atomic configurations about or within the defect, but there has been to date very little specific modeling of just which atoms move where for the III-V compound semiconductors.

Levinson *et al.* have reported[3,4] a defect in electron irradiated InP that exhibits this large lattice relaxation phenomenon to a particularly large degree and which they denote as the metastable M center. They have performed extensive measurements to characterize the M center and have presented a detailed description of the electronic level scheme of the defect complex in each of two distinct atomic configurations, which they have demonstrated belong to one and the same complex.[3–6]

In this paper we propose a specific atom model for the M center which we find accounts for the properties determined by Levinson *et al.* We assert that the large lattice relaxation which converts the M center from one configuration to the other is simply cation vacancy, V_{In}, nearest neighbor hopping, i.e., movement of a P atom from a site on its own sublattice to an adjacent V_{In} (vacant site on the In sublattice), or the reverse of this. We argue that either of these two configurations can be stable depending upon the position of the Fermi level E_f. We review evidence that vacancy nearest-neighbor hopping is a common mode of host atom diffusion in III-V compound semiconductors[7–10] and suggest that the model we propose for the M center in InP also accounts for large lattice relaxation behavior in several other defect complexes in III-V compound semiconductors.

II. M CENTER: A REVIEW OF THE EXPERIMENTAL INFORMATION

The metastable defect complex that is denoted as the "M center" has been observed in n-type InP only after electron irradiation.[3–6] The electron energy in these experiments was 1 MeV. This center was characterized by deep-level transient-spectroscopy (DLTS) and thermally stimulated capacitance (TSCAP) measurements, both in the dark and with optical excitation. Additionally, photoionization rates as a function of photon energy were experimentally determined.

The key result was that two distinctly different DLTS and TSCAP spectra were obtained from one and the same complex depending upon whether the sample had been cooled *without an applied bias* (configuration A) or had been cooled *with a reverse bias applied* (configuration B). Restating this distinction, for the A configuration the Fermi level E_f in the junction region of the DLTS test structure (where the defects are probed) is near the conduction-band edge E_c, while for the B configuration E_f at the junction is near the valence-band edge E_v in that region while the junction is cooled just prior to test. The B configuration actually occurs in two variants which differ in the thermal activation energy of one of their transitions by 50 meV. No corresponding variant of the A configuration has been reported. Figure 1 shows these two DLTS and TSCAP spectra reported in Refs. 3 and 6. Note that the DLTS and TSCAP experiments measure the emission of electrons e^-'s from filled traps during sample warming with the junction reverse biased. For configuration B, the sample was shorted temporarily at the minimum temperature, $T=33$ K, to remove the reverse bias (to allow E_f to approach E_c) and thus to fill the traps with e^-'s at the onset of the test.

 ©1985 The American Physical Society

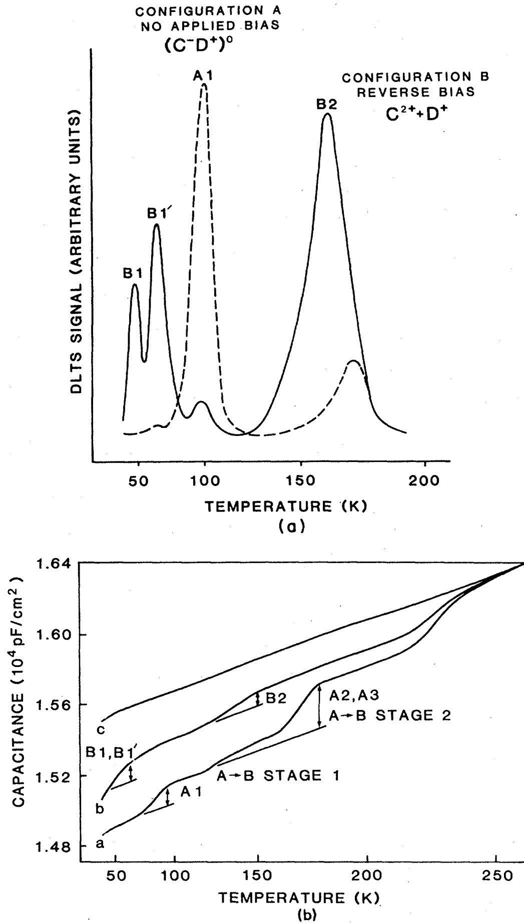


FIG. 1. (a) DLTS spectra for the A and B configurations of the M center. (b) TSCAP spectra of a, A configuration; b, B configuration; and c, a reference curve obtained in the B configuration but without reverse applied during the TSCAP scan period.

The major feature of the A configuration DLTS spectrum is an electron-emission peak from a donorlike center, denoted $A1$, with an activation energy of 0.15 eV and an electron-capture cross section $\sigma=9\times10^{-18}$ cm^2. The three large emission peaks of the B configuration all have $\sigma>2\times10^{-16}$ cm^2 (for electron capture). The thermal and optical ionization energies of the M center, as reported in Ref. 6, are displayed in Table I. $B1$ and $B1'$ denote values for the same transition of the two variants of the B configuration. Note that $B1'$ has about twice the amplitude of $B1$ in Fig. 1.

Annealing studies[4] (from 33 K to a little over 200 K) show that there is a reversible transformation between configurations,

$$A \Longleftrightarrow B \ . \tag{1}$$

The $A\rightarrow B$ transformation occurs with the $A3$ emission of Table I, which may be activated either optically or thermally. Two e^-'s are emitted simultaneously in this event. For the 123 s^{-1} DLTS rate window used in Refs. 3, 4, and 5, its rate R and characteristic temperature T are:

TABLE I. M-center ionization energies (Ref. 6).

Peak	Thermal (eV)	Optical (eV)
$A1$	0.15	<0.4
$A2$	0.42	0.68
$A3$	~0.42	>1.1
$B1$	0.09	<0.4
$B1'$	0.14	<0.4
$B2$	0.37	0.61

$$R(A\rightarrow B)=10^{11}\exp[(-0.42\text{ eV}/kT)]\text{ s}^{-1}\ ,$$
$$T(A\rightarrow B)=160\text{ K}\ . \tag{2}$$

The $B\rightarrow A$ transformation occurs as:

$$R(B\rightarrow A)=10^{7}\exp[(-0.24\text{ eV}/kT)]\text{ s}^{-1}\ ,$$
$$T(B\rightarrow A)=140\text{ K}\ . \tag{3}$$

Three e^-'s are captured in this event.

The $A\rightarrow B$ transition can be induced, even for $T<33$ K, by sub-band-gap photon irradiation provided that the photon energy, $h\nu\geq0.8$ eV, or by hole injection. It seems not to matter whether the holes are induced with photons of $h\nu$ greater than the band gap, $\Delta E_{cv}=1.35$ eV, or by forward bias injection. However, the $B\rightarrow A$ transition is not induced by photons of any wavelength nor by hole injection in any of the reported experiments.

Levinson *et al.* propose[4] the following structure for the A and B configurations:

$$A=(C^-D^+)^0 \tag{4}$$

(for the case of no bias applied while cooling, i.e., $E_f\sim E_c$) and

$$B^{3+}=C^{2+}+D^+ \tag{5}$$

(for the case that a reverse bias is applied during cool down, i.e., $E\sim E_v$). They have also concluded that in (4) and (5), C is an intrinsic defect or defect complex and that D is a shallow donor defect that remains ionized even at 33 K in the configuration B. The parentheses enclosing C^-D^+ are intended to indicate that this complex is stabilized by the Coulomb interaction between the ionized defect and the shallow donor.

The fact that two e^-'s should be emitted simultaneously at $A3$ is notable and has been claimed[4–6] to be evidence of "negative-U" character. We wish to explore this interpretation. For a second e^- to be emitted at essentially the same time as the first, either the second ionization potential $E_{t,2}$ of the trap must be much closer to E_c than the first or there must be some correlation between the states they occupied. Otherwise there would be a delay proportional to $\exp[-(E_c-E_{t,2})/kT]$ between the two emissions. The second ionization potential of a trap might be expected to be greater than the first due to the Coulomb interaction between the second carrier to be removed and the compensating charge left by the removal of the first. However, covalent bonding implies strong correlation and exchange effects among the valence electrons. [This is the reason that chemists who follow the convention of G. N. Lewis denote a covalent bond with two dots to indicate

that two electrons (one spin up and the other spin down) which are shared by the two atoms engaging in the bond in a wave function formed by the coherent overlap of one atomic orbital from each of these atoms.[11]] It can happen that the sum of the Coulomb, correlation, and exchange interactions, which is denoted as U, can be negative.[12] $U<0$ implies that a state associated with a particular bond will contain either two spin paired electrons or none; then the one electron, unpaired spin, bond is not stable. Although this situation is expected to be less common in crystals, because of the greater degree of resonance among atomic orbitals,[11] than in molecules, the negative-U property has been observed[13–15] for interstitial B, (B_i) in Si and for Si vacancies, V_{Si}. Due to the loss (or gain) of two e^-'s from (or into) a localized bond, one must expect that a negative-U situation is concomitant with a large rearrangement of the lattice during the transformation of the complex. (By convention, such rearrangements are called lattice relaxations.)

We propose a simpler correlation between the defect states to account for the simultaneous emission. Rather than an esoteric discussion of exchange and correlation of defect wave functions, we propose that one of the anion atoms surrounding a cation vacant site within the defect complex hops into that site, which in a III-V-compound crystal, converts a single acceptor cation vacancy into a donor anion vacancy and a donor antisite defect of the anion on the cation lattice site. This is a natural consequence of the fact that vacancy nearest-neighbor hopping is a common, and often dominant, mode of host atom diffusion in III-V-compound crystals.[7–10] Further consequences of this fact are discussed in the following paper.[16]

Let us summarize the facts with which any atomic model of the M center must be consistent.

(1) The M center is not found in unirradiated samples.

(2) The low introduction rate of the M center suggests that it is an intrinsic defect complex.

(3) The transformation between configurations A and B involves exchange of three e^-'s.

(4) The B configurations has two variants, B and B' and there seem to be twice as many of the B' as the B, while the A configuration seems to be unique.

(5) The B configuration remains ionized even at 33 K implying that part of the defect complex in the B configuration is a very shallow donor.

(6) The optical and thermal ionization energies given in Table I were observed.

(7) The σ's of the B configuration are of the order of an atomic geometrical cross section while that for $A1$ is distinctly less.

(8) $A \rightarrow B$ transformations can be initiated at low temperature by minority carriers or sub-band-gap radiation the while $B \rightarrow A$ transformation is immune to these activation processes.

III. WHAT DOES 1-MeV ELECTRON IRRADIATION INTRODUCE?

Let us first consider the implication of the fact that the M center was not found in unirradiated InP. Although precise measurements of the stoichiometry of the InP in question are not available, we assume it is similar to that of GaP. Very precise, Coulombmetric titration measurements of the stoichiometery of GaP showed[17] that even though samples were grown under widely varying conditions, all were P lean and most contained Ga microprecipitates. This is a consequence of the high vapor pressure of P at growth temperatures and the fact that the enthalpy of formation ΔH_f of V_P is less than that of V_{Ga}.[18,19] The same considerations cause us to assume that the as-grown InP in question is also P lean. The nonstoichiometric defects consistent with the InP being P lean include[18,19] V_P, In_P, In interstitials (In_i) and the complex $V_{In}In_P$ that is formed if a V_P hops to a nearest-neighbor site. We assume that the M center is something other than these.

The maximum energy T_M that can be transferred from an irradiating electron of energy E to an atom of mass M_A is given by relativistic mechanics to be

$$T_M = 2\frac{m}{M_A}\frac{E+2mc^2}{mc^2}E \, , \tag{6}$$

where m is the free electron mass and c is the speed of light. Thus, the 1-MeV electron can transfer 37.6 eV to an In atom or 139 eV to a P atom. These values are well above the estimated values[19] of the displacement energies to make vacancy-interstitial pairs in InP, which are 12.2 eV for In displacement and 16.5 eV for P displacement. We conclude that the irradiation introduces, as primary defects that were not present in the as-grown material, P_i and V_{In}. V_P and In_i must also be introduced, but the V_P were likely present before irradiation and most of the In_i probably add to In microprecipates that also were already present.

However, the second empirical fact we noted was that the introduction rates indicate that the M center is not a primary radiation defect. Furthermore, we do not expect[19–22] either P_i or V_{In} to remain as simple point defects during and after the irradiation process. It is well established that point defects, particularly interstitials, are mobile during such processes, and seem to diffuse athermally as a consequence of the ionization concomitant with the radiation.[23] Some fraction of the P_i will encounter V_{In}'s, particularly because the normal ionization states of these are[19] $P_i{}^{+n}$ where n is likely 2 or 3, and $V_{In}{}^-$. Thus, there is Coulombic attraction between them and the P_i tend to occupy the vacant In lattice site to produce an antisite defect P_{In} with a substantial release of energy.[19] While more energy would be released if the P_i would occupy the vacant site of a V_P; this process is somewhat inhibited by the Coulomb repulsion between $P_i{}^{+n}$ and $V_P{}^+$, the normal ionization state of V_P. Therefore, we conclude the first step in the production of the M center is likely to be

$$P_i + V_{In} \rightarrow P_{In} \, . \tag{7}$$

We note that a reaction in GaP that produces Ga_P, which were not at observable concentration before electron irradiation, has been reported[24] by Newman.

However, the M center contains at least two point defects and the isolated antisite is not likely to undergo any major lattice relaxations, so we must consider further. Once P_{In}'s have been formed during the irradiation process, they will become attracting centers for more $V_{In}{}^-$

because they will be ionized as either P_{In}^{+2} or as P_{In}^{+}. Indeed, early consideration of vacancies grown into III-V compound semiconductors lead to the conclusion[20,21] that their most common fate is to form complexes of an antisite defect with either one or two vacancies on second-nearest-neighbor sites on either side. This conclusion has been supported by direct lattice imaging electron microscopy[25] and other methods that, e.g., identify[22–27] the EL2 defect in GaAs as a family of complexes based upon $V_{Ga}As_{Ga}V_{Ga}$. We would expect some V_{In}^{-}'s also to become bound with V_P^{+}'s; we return to this point later. Therefore, let us consider the proposition the *M* center is, in one of its two configurations, the $V_{In}P_{In}$ complex, which is consistent with the first two facts noted above.

IV. AN ATOMIC MODEL FOR THE *M* CENTER

Our atomic model for the *M* center is shown in Figs. 2(a)–2(c). We make the following simple associations, which are consistent with facts (3) and (4) noted above.

$$A = V_{In}^{-} + P_{In}^{+} , \tag{8}$$

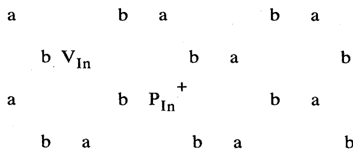
$$B = P_{In}^{+} + V_P^{+} + P_{In}^{+} . \tag{9}$$

Thus, for both *A* and *B* we take the more stable point defect *D* to be

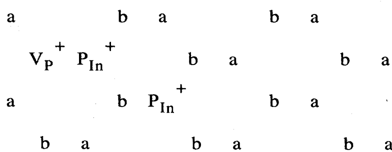
$$D = P_{In} , \tag{10}$$

⊕ (111); → (111)

(a) A Configuration



(b) B Configuration



(c) B' Configuration

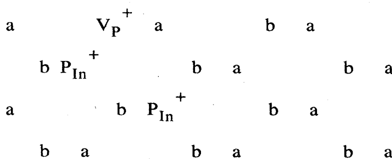


FIG. 2. Atomic model for the *M* center in electron-irradiated InP. (a) In *A* configuration, which is unique; (b) in *B* configuration variant, which is unique; and (c) in *B'* configuration variant, for which is another equivalent form with the V_P out of the plane but on the same ring as the other two defects.

and we take the point defect which exhibits the large lattice relaxation *C* to be

$$C(A) = V_{In} \tag{11}$$

in the *A* configuration and, in the *B* configuration,

$$C(B) = P_{In}V_P . \tag{12}$$

For the *B'* variant [Fig. 2(c)] we have all three defects on the same sixfold ring, while for the *B* variant [Fig. 2(b)] we have the V_P further from the initial P_{In} on a different ring. V_{In} and V_P are expected to be singly ionized as an acceptor and a donor, respectively.[18,19] The best theoretical values for antisite defect ionization levels[28] and experimental values for vacancy ionization levels[29] in InP available to us are displayed in Fig. 3. These are the same values that we recently used in our treatment of the InP metal-insulator-semiconductor field-effect transistor (MISFET), drift problem.[30]

Our formulation of *B* possesses the +3 charge state for E_f lower than about $E_v + 1.0$ eV, as required. Temkin *et al.* give[29] the empirical value of the donor ionization potential, i.e., the difference between E_c and the ionization level, as

$$\Delta E_{0/+}(V_P) = 0.36 \text{ eV} . \tag{13}$$

The *B*2 electron emission line is within 0.01 eV of this assignment. Buisson *et al.* take[28] the wave function of the least bound electron in the neutral state of the isolated antisite defect P_{In}^{0} to be effective-mass-like. Therefore, we assume the ionization energy for P_{In}^{+} can be greater than the effective mass value, 0.007 eV, by only a typical chemical shift. Thus, we estimate

$$B0 \equiv \Delta E_{0/+}(P_{In,1}) < 0.03 \text{ eV} , \tag{14}$$

which is sufficiently shallow to explain the ionization of the *B* configuration at 33 K [as required by fact (5) above].

The second ionization step of the *B* configuration has an activation energy either E_{B1} (=0.09 eV) for the *B* variant, or $E_{B1'}$ (=0.14 eV) for the *B'* variant. We ascribe this to the ionization of the second P_{In} in the complex. We argue that this ionization energy is greater than the effective mass value, 0.007 eV, and equal to the observed

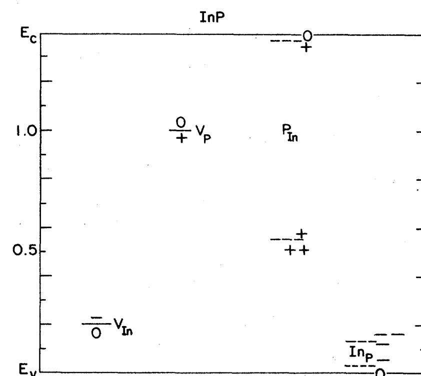


FIG. 3. Literature values (Refs. 28 and 29) for the ionization levels of vacancies and the antisite defects in InP.

values due to the combined action of two effects which work in opposite directions: (i) the second P_{In} has a P_{In}^{+} second nearest neighbor, which drives the level down from E_c by Coulomb interaction; but (ii) it also has a V_P first nearest neighbor, which is neutral at the time the $B1$ or $B1'$ transition occurs, and which drives the level up toward E_c due to its short range (donor-type) potential.

We now consider the relative intensity of the $B1$ and $B1'$ peaks in Fig. 1 and the source of the 50-meV difference between them. In Fig. 2, it is seen that the $A \rightarrow B$ transition occurs when one of the four P atoms about the V_{In} hops into that vacant site. (Only three b sites are shown in our two-dimensional representation.) One of these four P atoms is the next nearest neighbor to the initial P_{In}^{+}, while two others (only one of which is shown) are third nearest neighbors to the P_{In}^{+} and one is a fourth nearest neighbor. We do not expect the P atom that is the first nearest neighbor to be the one to make the hop; the resulting complex would then have two P_{In}^{+} separated only by a vacant site, so that the dielectric screening that normally is present would be absent and the Coulomb repulsion would be prohibitive. (The vacancy is, after all, a void in the dielectric.) Rather, we expect that either one of the third- or the fourth-nearest-neighbor P atom will be the one to hop. Since there are two third-nearest-neighbor P atoms and only one fourth-nearest-neighbor P atoms that can make the transition, the association of the third-nearest-neighbor variant with B' is consistent with fact (4), the observation that $B1'$ has about twice the magnitude of $B1$ in Fig. 1. We must speculate that the presence of the V_P^0 on the same ring, closer to the line between the two P_{In}^{+}'s increases the Coulomb repulsion between them more than in the fourth nearest neighbor case, where the V_P^0 is on the far side and that this accounts for the 50-meV difference between E_{B1} and $E_{B1'}$. We conclude that the association

$$E_{B1} \equiv \Delta E_{0/+}(P_{In,2,B}) = 0.09 \text{ eV} \quad (15a)$$

and

$$E_{B1'} \equiv \Delta E_{0/+}(P_{In,2,B'}) = 0.14 \text{ eV} \quad (15b)$$

is appropriate.

The isolated P_{In} is also expected to have a doubly ionized charge state P_{In}^{2+}. Buisson *et al.* estimated[28] this second ionization potential to be

$$\Delta E_{+/++}(P_{In}) = 0.78 \text{ eV} . \quad (16)$$

We regard the agreement between this value and the optical ionization energies $A2 = 0.68$ eV and $B2 = 0.61$ eV to be quite satisfactory within our model and make this association. Finally, Temkin *et al.* give[29] the empirical acceptor ionization energy for V_{In} to be 1.15 eV below E_c. The deionization of this acceptor state by photoexcitation of holes from the valence band would not have occurred in the photoionization experiments[3–6] because any holes that may have been in the junction must have been near E_v, which is only 0.2 eV below the acceptor level, and the minimum photon energy employed was 0.4 eV. Consequently, we have

$$\Delta E_{-/0}(V_{In}) = 1.15 \text{ eV} , \quad (17)$$

which is consistent with the $A3$ optical ionization peak. We summarize our account of the optical ionization peaks in Table II and conclude that these are consistent with fact (6) above.

Because $\Delta E_{0/+}(V_P) < \Delta E_{+/++}(P_{In})$, the V_P^{+} will be more stable in the reverse biased junction than the P_{In}^{++} would be. The Coulombic interaction between the V_P^{+} localized state and the localized P_{In}^{++} on the nearest neighbor sites should drive the P_{In}^{2+} level even closer to E_v. Consequently, we do not expect the P_{In}^{++} state, which would put the B configuration into a $+4$ state, will be attained in the DLTS or TSCAP experiments. We do expect the defects comprising this complex each to be singly ionized after e^- emission. Furthermore, the trapping cross sections σ of these three levels, being singly ionized donors in the initial state, are expected[30,31] to be of order the geometrical cross sections, or larger, which is consistent with fact 7, the observation that all are greater than 2×10^{-16} cm^2.

We can account for the $A1$ emission about equally well in either of two ways; a choice will require information about the experiment that is not available to us. References 3 and 4 lead us to understand the complex is neutral before the emission, but Ref. 6 tells us this is not established. It is also not indicated how many holes may be present in the reverse biased junction under the test condition; it might be that the $A1$ occurs by hole capture rather than by electron emission.

In the case that $A1$ occurs by electron emission, we take the initial state to be $V_{In}^{-}P_{In}^{0}$. Then the $A1$ emission results from the $0/+$ ionization level of the P_{In} and we have the repulsion from the deep level V_{In}^{-} to account[30,31] for the electron-capture cross-section value, 9×10^{-18} cm^2, distinctly less than a geometrical value, as required by fact (7). However, the thermal activation energy of $A1$, 0.15 eV, is somewhat greater than the $B0$, effective-mass value, whereas one would expect the Coulomb interaction of V_{In}^{-} with the effective-mass-like state of P_{In}^{0} to push its ionization level closer to E_c. To explain the fact of the $A1$ level position, we note that the ionization level of V_{In} is so shallow and $\Delta E_{c,v}$ is so large that the short ranged vacancy potential, which is attractive to e^-'s, should almost bind a second e^-; i.e., there should be a $--/-$ level just above E_c. We know that the single vacancy in Si does have a second acceptor ionization level[32] below E_c and Si has a smaller band gap. We infer that the short-range potential of the V_{In} causes this $0/+$ level to drop into the gap from an unperturbed

TABLE II. Association of optical peaks.

Peak	Model transition	Model value (eV)	Observed (eV)
$A1$	P_{In} $0/+$	~0.1	<0.4
	V_{In} $-/0$	0.2	<0.4
$A2$	P_{In} $+/++$	0.78	0.68
$A3$	V_{In} $-/0$	1.15	>1.1
$B0$	$P_{In,1}$ $0/+$	<0.03	<0.4
$B1$	$P_{In,2,B}$ $0/+$	~0.09	<0.4
$B1'$	$P_{In,2,B'}$ $0/+$	~0.14	<0.4
$B2$	P_{In} $+/++$	0.78	0.61

value near $B0<0.03$ eV to $A1=0.15$ eV. Thus it is that we have a "deep level," i.e., one produced largely by a local potential, which is rather near E_c, and has a small σ. An elaborate computer calculation, which is beyond the scope of this work, will be required to verify this last contention.

If on the other hand, there are some holes available because $E_f \sim E_v$ in the reverse biased junction, then we assume the initial state is neutral, i.e., $V_{In}^- P_{In}^+$, and the transition occurs by hole capture to neutralize the acceptor level of the V_{In}, for which the activation energy given[29] by Temkin is 0.2 eV. This would seem to be close enough to $E_{A1}=0.15$ eV without any adjustments. The low value inferred for the capture cross section would then be an artifact of the assumption that the process was electron emission when in fact it was hole capture, but with a low density of holes.

We have invoked P-atom nearest-neighbor hopping into the In vacancy as the atomic mechanism responsible for the $A \rightarrow B$ transformation (see Fig. 2). Movement of the P atom into the In vacancy creates a second P_{In} antisite defect and creates a V_P. Likewise, the $B \rightarrow A$ transformation would occur by P hopping from the P_{In} nearest neighbor into the V_P. We have previously estimated,[30] using the simple ballistic model of atomic diffusion,[33] the activation barrier for P nearest-neighbor hopping as 0.3 eV. Our model associates this value with the thermal activation energies that Ref. 6 gives for the $A \rightarrow B$ direction as $E_{A3}=0.42$ eV and for the $B \rightarrow A$ direction as the 0.24 eV in Eq. (2). We summarize our account of the thermal activation energies in Table III and conclude that our model is completely consistent with fact (6).

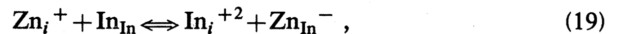
V. OTHER EVIDENCE OF VACANCY NEAREST-NEIGHBOR HOPPING

We feel that the vacancy nearest-neighbor hopping mode, with the concomitant transformation of a single acceptor V_{In}^- to a single donor V_P^+ to account for the simultaneous emission of $2e^-$ (which Stavola *et al.* call[5,6] "negative U" character), is a very natural supposition in view of what is known about self-diffusion in III-V compound semiconductors. Our present argument is similar to that used to account for the InP MISFET drift problem.[30] In that situation (in unirradiated material), V_P's are the predominant nonstoichiometric defect present and the field-induced transformation is

$$V_P^+ + 3e^- \Longleftrightarrow V_{In}^- In_P^- \ . \tag{18}$$

This takes place by the hopping of an In atom with an activation energy of about 1.2 eV. We note that our theory of the MISFET problem has been supported by the recent observations[30] of Pande and Gutierrez that the problem can be suppressed by co-deposition of P with the SiO_2 gate insulator.

We know that vacancy nearest-neighbor hopping is a common, often dominant, mode of host atom diffusion in III-V compound semiconductors from observations of the enhancement of host interdiffusion in superlattice structures that is dramatically enhanced[7-10] by the introduction of Zn interstitial donors, Zn_i^+. This was explained[7] in terms of the electrostatic interaction between the Zn_i^+'s and the antisite defect-vacancy complexes, e.g., $V_P^- In_P^-$, that are present in the saddle-point configurations of such a diffusion mechanism. (By reducing the total energy of the saddle-point configuration, this interaction reduces the activation barrier by a few eV and thereby dramatically increases the rate of this diffusion process.) The conclusive point in this question was that a similar degree of enhancement was found[7,8] on both the anion and the cation sublattice. If the mechanism of the enhancement had been replacement of the host cations by the Zn_i, e.g.,



$$Zn_i^+ + In_{In} \Longleftrightarrow In_i^{+2} + Zn_{In}^- \ , \tag{19}$$

then there would have been essentially no enhancement of the host anion diffusion because Zn almost never resides on the anion sublattice. Similarly, if the mechanism of enhancement had involved interaction of divacancy complexes with the Zn_i^+, then a little consideration[7] shows that the effect would have been confined to the anion sublattice. In Ref. 7 it was shown that nearest-neighbor hopping of anion vacancies causes two-thirds as much diffusion on the anion sublattice as on the cation sublattice whether or not it is enhanced with Zn_i^+. Although we do not know of a similarly decisive demonstration that cation vacancies commonly diffuse by nearest-neighbor hopping, it is difficult to construct an argument that they should be different.

VI. DEFECT ENTHALPIES OF FORMATION AND HOLE INDUCED TRANSFORMATION

Consider now the enthalpies of formation ΔH_f of vacancies and antisite defects in InP. Handbook values[19] for the neutral species are displayed in Table IV. It follows from these values that the reaction

$$V_{In}^0 \rightarrow V_P^0 + P_{In}^0 \tag{20}$$

would release 0.45 eV of energy and thus should occur spontaneously.

TABLE III. Association of thermal activation energies.

Peak	Model transition	Model value (eV)	Observed (eV)
$A1$	P_{In} 0/+	~0.1	0.15
	V_{In} −/0	0.2	0.15
$A2$	$V_{In} \rightarrow P_{In}V_P$	0.3	0.42
$A3$	$V_{In} \rightarrow P_{In}V_P$	0.3	0.42
$B0$	$P_{In,1}$ 0/+	<0.03	<0.03
$B1$	$P_{In,2,B}$ 0/+	~0.09	0.09
$B1'$	$P_{In,2,B'}$ 0/+	~0.1	0.14
$B2$	V_P 0/+	0.36	0.37
$B \rightarrow A$	$V_P P_{In} \rightarrow V_{In}$	0.3	0.24

TABLE IV. Enthalpies of formation of point defects (in units of eV).

$\Delta H_f(V_{In}^0)=2.74$
$\Delta H_f(V_P^0)=1.87$
$\Delta H_f(P_{In}^0)=0.42$
$\Delta H_f(In_P^0)=0.89$

However, the enthalpy of formation of any of the charged states of any defect is dependent upon the position of E_f. We continue to assume that the ionization levels given in Fig. 3 are appropriate for V_P and for P_{In} in our model of the *M*-center complex. Then, there is no position of E_f for which both V_{In} and V_P would be in their neutral ionization states at low *T*. Indeed, if we combine the values of the ionization levels in Fig. 3 (for isolated levels) with the ΔH_f's in Table IV, we conclude that the value of E_f for which the ionized states of the $V_{In} \Longleftrightarrow P_{In}V_P$ defect are equally likely at $T=0$ is $E_f = E_v + 1.0$ eV. For such a value of E_f at $T=0$, the ionization state of the V_{In} configuration would be V_{In}^- and the value of $\Delta H_f(V_{In}^-)$ would be 0.8 eV less than $\Delta H_f(V_{In}^0)$ because an electron obtained from the Fermi sea at E_f would fall into the acceptor ionization level at $E_v + 0.2$ eV. The ionization state of the $V_P P_{In}$ configuration would be $V_P{}^0 P_{In}{}^+$. The ΔH_f of this ionized complex would be reduced from the neutral value by 0.35 eV because a hole from the Fermi sea would go to the first-donor ionization level of P_{In} which is very near E_c. Thus we have that the state of lower energy of the complex is the *A* configuration if the *n*-type sample is not reverse biased and the *B* configuration if it is biased. This too is consistent with observation. The fact that both the *A* and *B* configurations can be regained by heating the sample is a simple consequence of the small activation energy, ~ 0.3 eV, of the process.

Let us now answer the question why the $A \rightarrow B$ reaction can be induced by photoexcitation or minority carrier injection but the $B \rightarrow A$ reaction cannot. In our model (Fig. 2), the *A* configuration can bind any holes that encounter it by neutralizing the V_{In}^-. The cross section for such trapping is large because the level is close to E_v. The P_{In}^+ can also trap e^-'s, which are the majority carriers, with a large cross section, and this would neutralize the antisite defect. However, once both constituents of the *A* configuration have been neutralized, Eq. (20) implies there will be a rapid and spontaneous conversion to the *B* configuration. Once the *M* center is in the *B* configuration, we doubt that it could bind another hole to reach the $+4$ charge state. Even if it did bind another hole and an electron, there is no mechanism evident in Fig. 2 by which either this bound exciton or its subsequent annihilation would drive one of the antisite defects into the vacancy, as would be required to form the *A* configuration. Therefore, we conclude that our model is also consistent with fact (8).

VII. CONTRIBUTIONS FROM DIVACANCIES

We noted above that some of the V_{In}^-'s produced during the electron irradiation may form pairs with V_P^+. If these are on third nearest-neighbor sites, we have the situation shown in Fig. 4(a), which would behave in the DLTS and TSCAP experiments in a manner similar in some respects to that of the *M* center. We denote this third-nearest-neighbor vacancy pair the A^* configuration. In Fig. 4(b) we show the B^* configuration which results when one of the P atoms neighboring the V_{In} hops into that vacant site, just as the analogous P-atom hopping

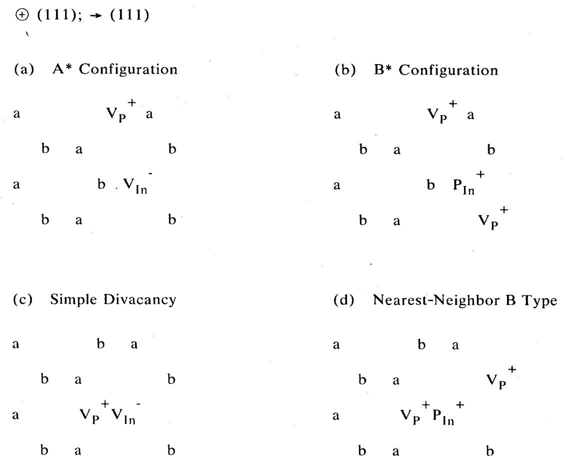


FIG. 4. A pair of vacancies could form an M^* center that would behave like the *M* center in many respects as long as they do not become first nearest neighbors. (a) The A^* configuration of the M^* center, compare to Fig. 2(a). (b) The B^* configuration of the M^* center, compare to Fig. 2(b) or 2(c). (c) The simple divacancy, which would be bound by the divacancy binding energy (Ref. 36) of order 0.9 eV. (d) The *B* configuration of the divacancy, which is unlikely to be found.

creates the *M* center *B* configuration. Several, but not all, of the features of the *M* center could be accounted for by this model of the "M^* center" because it also contains V_{In}, V_P, and P_{In} and transforms by P-atom nearest-neighbor hopping. In a preliminary publication[34] we suggested that this was the *M* center.

We propose that the M^* center can also be found in electron-irradiated InP provided the sample is quenched, i.e., cooled rapidly to the test temperature. The reason that quenching would be important is that the vacancy pairs would tend to approach to one of the first-nearest-neighbor sites and form a simple divacancy [see Fig. 4(c)]. In doing so, the pair would release the divacancy binding energy.[35,36] For InP this has been estimated[36] to be 0.87 eV. This value would have to be added to the activation energy of the moving P atom to give a total of 1.2 eV. With such a large activation energy it is doubtful the "*B* configuration of the divacancy" [Fig. 4(d)] would be seen, even with photoexcitation. The divacancy would probably remain atomically stable during the experiment.

VIII. CONCLUSIONS

We assert that the simple atomic model (Fig. 2) which we have presented, accounts for the data available[3–6] regarding the *M* center in electron-irradiated InP and further that it is the logical choice for what should be expected to result from the irradiation. We associate the simultaneous emission of two electrons during the $A \rightarrow B$ transition with the conversion of V_{In} to $P_{In}V_P$ by vacancy nearest-neighbor hopping, which we have noted is the common mode of self-diffusion in III-V compound semiconductors. It is, therefore, not necessary to speculate

about correlation and exchange effects among the defect wave functions which might be the source of negative U character.

The phenomena we have described and shown to be consistent with the data of Refs. 3 to 6 should be expected to occur in other III-V samples as well. We suggest that it is indeed responsible for several other examples of "large lattice relaxation."

---

[1]C. H. Henry and D. V. Lang, Phys. Rev. B **15**, 989 (1977).
[2]J. M. Langer, in *New Developments in Semiconductor Physics,* edited by F. Baleznay, G. Ferenczi, and J. Giber (Springer, Berlin, 1980), Vol. 122.
[3]M. Levinson, J. L. Benton, and L. C. Kimerling, Phys. Rev. B **27**, 6216 (1983).
[4]M. Levinson, M. Stavola, L. Benton, and L. C. Kimerling, Phys. Rev. B **28**, 5848 (1983).
[5]M. Stavola, M. Levinson, J. L. Benton, and L. C. Kimerling, Phys. Rev. B **30**, 832 (1984).
[6]M. Stavola, M. Levinson, J. L. Benton, and L. C. Kimerling, J. Electron. Mater. **14a**, 191 (1985).
[7]J. A. Van Vechten, J. Appl. Phys. **53**, 7082 (1982); **55**, 607 (1984).
[8]M. D. Camras, N. Holonyak, K. Hess, M. J. Ludowise, W. T. Dietze, and C. R. Lewis, Appl. Phys. Lett. **42**, 185 (1983).
[9]J. W. Lee and W. D. Laidig, J. Electron. Mater. **13**, 147 (1984).
[10]J. A. Van Vechten, J. Vac. Sci. Technol. B **2**, 569 (1984).
[11]L. Pauling and E. B. Wilson, *Introduction to Quantum Mechanics* (McGraw-Hill, New York, 1935), p. 377.
[12]P. W. Anderson, Phys. Rev. Lett. **39**, 953 (1975).
[13]G. A. Baraff, E. O. Kane, and M. Schlüter, Phys. Rev. B **21**, 3563 (1982).
[14]R. D. Harris, J. L. Newton, and G. D. Watkins, Phys. Rev. Lett. **48**, 1271 (1982).
[15]J. L. Newton, A. P. Chatterjee, R. D. Harris, and G. D. Watkins, Physica **116b**, 219 (1983).
[16]J. A. Van Vechten and J. F. Wager, following paper, Phys. Rev. B **32**, 5259 (1985).
[17]A. S. Jordan, A. Von Neida, R. Caruso, and C. K. Kim, J. Electrochem. Soc. **121**, 153 (1974); C. K. Kim, unpublished but available from A. S. Jordan, AT&T Bell Laboratories, Murray Hill, N.J. 07974.
[18]F. A. Kröger, *The Chemistry of Imperfect Crystals* (North-Holland, Amsterdam, 1964), p. 418.
[19]J. A. Van Vechten, in *Materials, Properties and Processes,* Vol. 3 of *Handbook on Semiconductors,* edited by S. P. Keller (North-Holland, Amsterdam, 1980), Chap. 1.
[20]J. A. Van Vechten, J. Electrochem. Soc. **122**, 423 (1975).
[21]J. A. Van Vechten, J. Electrochem. Mater. **4**, 1159 (1975).
[22]J. A. Van Vechten, J. Phys. C **17**, L933 (1984).
[23]J. C. Bourgoin and J. W. Corbett, Radiat. Eff. **36**, 157 (1978).
[24]R. C. Newman, J. Electron. Mater. **14a**, 87 (1985).
[25]J. B. Van der Sande and E. T. Peters, J. Appl. Phys. **46**, 3689 (1975).
[26]Y. Zou, J. Zhou, Y. Lu, K. Wang, and C. Sheng, J. Electron. Mater. **14a**, 1021 (1985).
[27]E. R. Weber, J. Electron. Mater. **14a**, 7 (1985) and therein.
[28]J. Buisson, R. E. Allen, and J. D. Dow, Solid State Commun. **43**, 833 (1982).
[29]H. Temkin, B. V. Dutt, and W. A. Bonner, Appl. Phys. Lett. **38**, 431 (1981).
[30]J. A. Van Vechten and J. F. Wager, J. Appl. Phys. **57**, 1956 (1985); see also K. P. Pande and D. Gutierrez, Appl. Phys. Lett. **46**, 416 (1985).
[31]M. Lax, J. Phys. Chem. Solids **8**, 66 (1959).
[32]G. D. Watkins, *International Conference on Lattice Defects in Semiconductors, Freiburg, Germany, 1974* (IOP, London, 1975), p. 1 and especially p. 13.
[33]J. A. Van Vechten, Phys. Rev. B **12**, 1247 (1975).
[34]J. F. Wager and J. A. Van Vechten, Bul. Amer. Phys. Soc. **30**, 417 (1985).
[35]L. J. Cheng, J. C. Corelli, J. W. Corbett, and G. D. Watkins, Phys. Rev. **152**, 761 (1966).
[36]J. A. Van Vechten, Phys. Rev. B **11**, 3910 (1975).