

## Divacancies in the Ga-related III-V compound semiconductors: Electronic structure and charge states

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We report on theoretical calculations for the electronic structure of the divacancies at different charge states in the three Ga-related III-V compound semiconductors, GaP, GaAs, and GaSb, based on a self-consistent tight-binding theory. The calculations are done with the use of the recursion method and the supercell approximation. We show that the divacancies can have many charge states. We calculate the energy positions and localizations of the defect levels for the predicted charge states. We find that each divacancy at a charge state introduces seven defect levels, three at the edges of the lower gap and four in or around the fundamental band gap. We present a molecular-orbital treatment of the four fundamental gap-related defect levels. We also find that the two defect levels in the lower half of the fundamental band gap stay at close energies and have an energy ordering that is dependent on the charge state of the defect. We critically compare the results of our calculations with experiments and other theoretical calculations. We argue that in the calculations for the divacancies in the III-V compound semiconductors, it is important to eliminate the self-interactions from the self-consistent defect potentials.

### I. INTRODUCTION

Vacancy defects in III-V compound semiconductors are among the fundamental defects and can exist in both sublattices. Using the electron-paramagnetic-resonance (EPR) technique, the identifications of the neutral cation vacancy  $V_{\text{Ga}}^0$  in GaP,<sup>1</sup> the doubly negatively charged cation vacancy  $V_{\text{Ga}}^{2-}$  (Ref. 2) and the singly negatively charged anion vacancy  $V_{\text{As}}^-$  (Ref. 3) in GaAs, and the neutral anion vacancy  $V_{\text{P}}^0$  in InP (Ref. 4) have been reported. Studies of many vacancy defects in GaP, GaAs, and InP by the positron-annihilation technique<sup>5-11</sup> have also been performed (for a review see Ref. 12). These positron-annihilation studies clearly indicate that an anion vacancy introduces a defect level into the upper half of the fundamental band gap, while a cation vacancy introduces a defect level into the lower half of the gap. This result has also been obtained in a number of theoretical calculations.<sup>13-17</sup> As a consequence, for the Fermi level at a middle gap position the cation (anion) vacancy in one of these III-V compound semiconductors is to be negatively (positively) charged. Therefore, the two vacancies attract each other, increasing the probability to form a divacancy.

Detailed experimental studies on the electronic structure of the divacancies in III-V compounds have not been reported. However, we are aware that, in the studies of the defects in GaAs by the positron-annihilation technique,<sup>6,7</sup> an increase in the positron lifetime was suggested to be associated with the divacancy. Furthermore, from an analysis of kinetic and equilibrium thermal data on the native deep donor, *EL2*, in GaAs in a wide temperature range (roughly 700–1200°C), Morrow has recently demonstrated that the divacancy is one primary defect and plays an important role in the formation of *EL2* in GaAs.<sup>18</sup> Theoretically, a local-density calculation

for the electronic structure of the divacancy in GaAs,<sup>19</sup> a self-consistent semiempirical tight-binding calculation for the divacancy in InP,<sup>20</sup> and a non-self-consistent tight-binding calculation for the divacancies in GaAs, GaP, AlAs, InP, and InAs (Ref. 21) were reported. In the first two calculations, the charge states of the divacancy in GaAs and InP were studied and the complex nature of the electronic structure of the divacancy defects was revealed.

In this work, we report on the calculations of the electronic structure for the undistorted divacancies at different charge states in three Ga-related III-V compound semiconductors, namely GaP, GaAs, and GaSb. The calculations are done with the use of a self-consistent tight-binding theory, the recursion method (a real Green's-function method),<sup>22,23</sup> and the supercell approximation.<sup>24</sup> These calculations complement our recent works on the electronic structure of the neutral and charged isolated vacancies in the three compound semiconductors.<sup>15,16</sup> We will focus mainly on the defect-induced states around the fundamental band gap and the trend of their energy positions on the charge states. We will analyze the physical origin of these fundamental gap-related defect levels in terms of the broken-bond-like orbitals hung on the neighboring atoms of the divacancies. We will compare the results of our calculations with relevant experiments and other theoretical calculations.

### II. THEORETICAL METHOD

Our calculations are based on a self-consistent tight-binding theory with the use of the  $sp^3$  first- and second-nearest-neighbor Hamiltonians of Strehlow, Hanke, and Kühn for the perfect crystals,<sup>25</sup> the local charge-neutrality condition proposed by Xu and Lindefelt for the defect potential of the neutral isolated vacancies,<sup>15</sup>

the Sankey-Dow semiempirical model of Coulomb effects,<sup>26</sup> the Wolfsberg-Helmholz formula for the orbital interactions,<sup>27</sup> and a large supercell containing 1331 pairs of cation and anion atomic sites which is subject to periodic boundary conditions.<sup>24</sup> The theory has been successfully used to study many vacancy-related defects in semiconductors, such as the neutral and charged isolated vacancies in GaP, GaAs, and GaSb,<sup>15,16</sup> the neutral and charged isolated vacancies and divacancy in InP,<sup>20</sup> and the neutral vacancy-related defect complexes in Si.<sup>28</sup>

Formally, we can express the Hamiltonian for a divacancy defect as  $H = H_0 + U$ , where  $H_0$  is the Hamiltonian for the corresponding perfect crystal and  $U$  stands for the defect potential. In our calculations, nonzero elements contained in the matrix of the defect potential  $U$  are the diagonal matrix elements of the atoms at the vacant sites and at their first- and second-nearest-neighbor atomic sites, the off-diagonal matrix elements between the atoms at vacant sites and their first-nearest-neighbor atoms, and the off-diagonal matrix elements between the first-nearest-neighbor atoms of the vacant sites. We neglect any longer-ranged contributions to  $U$  since including these contributions can be expected only to result in some rather small and unimportant energy shifts in the energy levels of the defect (see the discussions presented in Sec. III C).

In the calculations for each divacancy, the diagonal matrix elements of the Hamiltonian  $H$  for the two vacant sites are taken to be infinite in magnitude and the off-diagonal matrix elements to be zero. However, the off-diagonal matrix elements between atoms adjacent to the divacancy are calculated from the bulk values of the first-nearest-neighbor interactions using the Wolfsberg-Helmholz formula<sup>27</sup> and the simplified Slater orbitals defined in Refs. 15 and 16. In order to fulfill the requirement that the quantitative theory of the electronic structure of the defects must incorporate the electron-electron interactions, the diagonal matrix elements of the Hamiltonian  $H$  have to be determined self-consistently. Therefore, in the present calculations, the diagonal matrix elements on the first- and second-nearest-neighbor atoms of the divacancy are modified so as to approach the self-consistency.

In our earlier works,<sup>15,16</sup> where we studied the electronic structure of the isolated cation and anion vacancy defects in GaP, GaAs, and GaSb, the diagonal matrix elements of the first- and second-nearest-neighbor atoms of the vacancies were self-consistently calculated for the defects at neutral charge states using a local charge-neutrality condition (Refs. 15 and 16). However, the local charge-neutrality condition may not be valid for the divacancy defects because their defect states are no longer isotropically localized on their first-nearest-neighbor atoms. Instead, approximate self-consistency is achieved in this work by using the Sankey-Dow semiempirical model of Coulomb effects in semiconductors<sup>26</sup> and the classic electrostatic Coulomb formula of the point charges.

The Sankey-Dow model has been used in a number of calculations for the point defects in semiconductors.<sup>15,16,26,29</sup> The essential feature of the model is that

the intra-atomic electron-electron interactions are easily taken into account and the self-interactions are well eliminated. However, for the divacancies, changes in the charges accumulated in the neighborhood of the defects can occur. These changes will result in energy shifts in the diagonal matrix elements due to the corresponding changes in the interatomic electron-electron interactions. In the calculations for the defect complexes in the semiconductors it might be necessary to take the variations in the interatomic electron-electron interactions into account, in order to simulate the effects of the interdefect electron-electron interactions. In the present calculations, the energy shifts in the diagonal matrix elements on both the first- and the second-nearest-neighbor atoms of the divacancies due to the intra-atomic electron-electron interactions are calculated with the Sankey-Dow model, while the shifts in the diagonal matrix elements on these atoms due to the interatomic electron-electron interactions are simply calculated with the classic electrostatic Coulomb formula for the point charges. It is clear that the diagonal matrix elements of the Hamiltonian  $H$  of a divacancy defect are functions of the orbital occupancies, which in turn are fully determined by the Hamiltonian  $H$ . Therefore, the procedure of the calculations should be repeated iteratively until self-consistency is obtained. In this work, the recursion method (a real Green's function method) developed by Haydock *et al.*<sup>22,23</sup> is used to go through this procedure and process the resulting self-consistent Hamiltonians.

Overall, a theory for calculations of the electronic structure of the divacancy defects in compound semiconductors has been outlined. Further details on the calculations of the self-consistent Hamiltonians of the vacancy-related defects and on the use of the recursion method can be found in our previous works (Refs. 15 and 16).

### III. RESULTS AND DISCUSSION

In earlier studies<sup>15,16</sup> we have shown that the isolated vacancies in GaP, GaAs, and GaSb can have many different charge states, and at each charge state each of the vacancies introduces a  $t_2$  gap level in the fundamental gap and an  $a_1$  level close to the lower edge of the gap. We have found that the  $t_2$  gap level associated with an isolated cation vacancy in one of the three Ga-related compounds is very well separated from the  $t_2$  gap level associated with an isolated anion vacancy in that compound. This is also true for the two isolated vacancies at charge states. Basically, the former level is located in the lower half of the fundamental band gap, and the latter one in the upper half of the gap. This characteristic feature of the isolated vacancies in the three Ga-related III-V compounds has also been obtained by local-density calculations<sup>13,14,17</sup> and has already been used in the interpretation of many experimental results of the positron-annihilation spectroscopy.<sup>12</sup> Therefore, one can expect that, with the Fermi level around the middle of the fundamental band gap, the isolated cation and anion vacancies in one of the three compounds will stay at opposite charge states and thus attract each other, increasing the probability to form the divacancy defects. Moreover, the

divacancy defects may also be directly created in these compounds by electron irradiation.<sup>30</sup>

### A. Qualitative model

In order to have a better understanding of the results of the calculations, we present here a qualitative model for the description of the electronic structure of the divacancy in a III-V compound semiconductor. We will mainly focus on the discussion of the defect states in and around the fundamental band gap. The model is shown in Fig. 1. In this model, these fundamental gap-related defect levels are described in terms of the broken-bond-like orbitals of the six first-nearest-neighbor atoms of the divacancy. In the absence of lattice distortions the symmetry point group of the divacancy is  $C_{3v}$  and the symmetrical linear combinations of the three equivalent broken-bond-like orbitals on the atoms adjacent to either the cation or the anion vacant site can be formed so that one component has  $a_1$  and the other two  $e$  symmetry [Figs. 1(a) and 1(c)], indicating that the divacancy can have two  $a_1$  and two  $e$  one-electron defect states in and around the fundamental band gap. When the orbital interactions are taken into account, the two  $a_1$  linear combinations are expected to form binding and antibinding

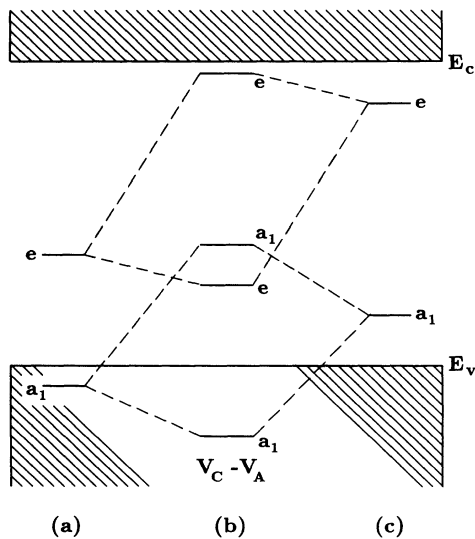


FIG. 1. Energy-level scheme of the undistorted divacancy in a Ga-related III-V compound semiconductor in terms of the six broken-bond-like orbitals centered on the first-nearest-neighbor atoms of the divacancy. The three broken-bond-like orbitals from either (a) the neighboring anion atoms adjacent to the cation vacant site or (c) the neighboring cation atoms adjacent to the anion vacant site can be symmetrized to form a nondegenerate  $a_1$  and a double degenerate  $e$  symmetric linear combinations. (b) The defect levels of the divacancy formed from the two sets of the symmetrized broken-bond-like orbitals under the consideration of the interactions between these two sets of orbitals. The effects of deviations from the broken-bond-like orbitals and of changes in distribution of the electron charges on the electronic structure of the divacancy are not taken into account in the figure.

nondegenerate  $\sigma$ -like defect states and the four  $e$  linear combinations are expected to give binding and antibinding  $\pi$ -like double-degenerate defect state. A schematical illustration of these defect states is shown in Fig. 1(b). Of course our model is an oversimplification, because (1) the wave functions of the electron defect states will also spill over somewhat onto the more distant neighbors, (2) not all  $p$ -like orbitals of the three neighboring cation or anion atoms of the divacancy are equivalent and thus the orbitals on these neighboring atoms are no longer as broken-bond-like as they are in the cases of the isolated vacancies, and (3) charge transfer between the two defect components of the divacancy will occur. The results of our calculations presented in the following subsections will show that the basic feature of the electronic structure of the divacancy defects is, however, indeed correctly predicted by the simple model, which directly leads us to note that neglecting the tails of the wave functions of the defect states in the model is justified. These results will also show that significant changes in the electronic structure of the defects, such as the ordering of these fundamental gap-related defect levels, indeed appear to be due to the presence of the deviations of the wave functions of the defect states from the broken-bond-like orbitals and the charge transfer between the two defect components of the divacancy. Therefore, the model presented in Fig. 1 should only be used for a primitive understanding of the electronic structure of the divacancies in the III-V compound semiconductors.

### B. Neutral state

In a previous work,<sup>31</sup> we have shown and discussed the electronic structure of the divacancies in GaP, GaAs, and GaSb at the neutral charge state. In that work, the diagonal matrix elements of the defect potential only of the first-nearest-neighbor atoms of a divacancy were self-consistently calculated, while the diagonal matrix elements of the second-nearest-neighbor atoms of the divacancy were simply fixed to the corresponding values calculated self-consistently for the neutral isolated vacancies. This is different from the present calculations, since in the present calculations we have calculated self-consistently the defect potential for all the atoms in the extended central cell of the divacancy defect, defined as a divacancy plus its six first- and eighteen second-nearest-neighbor atoms. However, from the present calculations we have found that for the divacancy at the neutral charge state the use of the self-consistently calculated defect potential for the second-nearest-neighbor atoms can give only the corrections to the calculated fundamental gap levels of the previous work<sup>31</sup> on the order of 0.01–0.03 eV. Thus our previous calculations<sup>31</sup> for the neutral divacancies are justified, and the discussions made in that work are applicable to the present work. Since the electronic structure of the divacancies at the neutral charge state was discussed in detail in that work, here we give only a summary of the present calculation results and some brief discussions.

In Table I, we have listed the results of the present calculations for the energy levels of the localized defect

TABLE I. Characteristic energy levels of the neutral divacancy in GaP, GaAs, and GaSb. The energies of the levels are measured relative to the top of the valence band. The width of the fundamental band gap  $E_g$  is 2.16 eV for GaP, 1.51 eV for GaAs, and 0.86 eV for GaSb, while the lower gap is between  $-7.09$  and  $-9.45$  eV for GaP, between  $-6.88$  and  $-9.68$  eV for GaAs, and between  $-6.76$  and  $-9.00$  eV for GaSb. All energies are in eV.

Defect	Near lower gap			Near fundamental gap			
	$a_1$ energy level	$e$ energy level	$e$ energy level	$a_1$ energy level	$e$ energy level	$e$ energy level	$e$ energy level
GaP: $(V_{\text{Ga}}-V_{\text{P}})^0$	-9.48	-6.96	-9.30	-0.02	0.55	0.55	1.85
GaAs: $(V_{\text{Ga}}-V_{\text{As}})^0$	-9.57	-6.76	-9.43	-0.34	0.30	0.30	1.34
GaSb: $(V_{\text{Ga}}-V_{\text{Sb}})^0$	-8.85	-6.58	-8.80	-0.29	0.17	0.17	0.81

states for the divacancy in GaP, GaAs, and GaSb at the neutral charge state. Seven localized defect states are found for each divacancy. Four of them (two  $a_1$  and two  $e$  defect states) are located in energies in and around the fundamental band gap (see the right side in Table I) and are referred to as the fundamental gap-related defect states, while the other three (two  $a_1$  and one  $e$  defect states) are located at the edges of the lower gap (see the left side in Table I). The four fundamental gap-related

defect states appear just as we expected in our model presented in Fig. 1. However, the remaining three states at the edges of the lower gap cannot be described by the model. To understand the physical origin of these three states, we recall that the isolated cation vacancy in a Ga-related III-V compound introduces an  $a_1$  and a  $t_2$  defect state in energies at the lower edge of the lower gap, and that the isolated anion vacancy introduces only an  $a_1$  defect state at the upper edge of the lower gap. Thus the

TABLE II. Calculated energy levels in the fundamental band gap and localizations ( $w$ ) of the levels on the neighboring atoms of defect for the divacancy ( $V_{\text{Ga}}-V_{\text{P}}$ ) in GaP at charge stages. The energies of the levels are measured relative to the top of the valence band. The subscripts 1 and 2 indicate, respectively, the localizations of the levels on the three equivalent first-nearest-neighbor atoms and on the nine equivalent second-nearest-neighbor atoms of the divacancy. The superscript  $C$  ( $A$ ) indicates the equivalent neighboring atoms at the lattice sites closer to the cation (anion) vacant site.  $w^{\text{ec}}=w_1^C+w_2^C+w_1^A+w_2^A$  indicates the localization of the levels on all the atoms in the defect extended central cell (defined as the two vacant sites plus the six first- and the eighteen second-nearest-neighbor atoms of the divacancy).  $Q^{\text{ec}}$  is the calculated net charge appeared in the extended central cell.

Charge state	Energy level (eV)	Symmetry	Energy level					$Q^{\text{ec}}$ ( $e^-$ )
			$w_1^C$	$w_2^C$	$w_1^A$	$w_2^A$	$w^{\text{ec}}$	
$(V_{\text{Ga}}-V_{\text{P}})^{3-}$	0.96	$a_1$	0.14	0.02	0.42	0.28	0.84	+0.06
	0.96	$e$	0.63	0.21	0.00	0.01	0.85	
	2.16	$e$	0.01	0.01	0.41	0.36	0.79	
$(V_{\text{Ga}}-V_{\text{P}})^{2-}$	0.77	$a_1$	0.23	0.04	0.37	0.22	0.86	+0.05
	0.91	$e$	0.62	0.21	0.00	0.01	0.85	
	2.05	$e$	0.01	0.01	0.46	0.36	0.84	
$(V_{\text{Ga}}-V_{\text{P}})^{1-}$	0.61	$a_1$	0.15	0.02	0.44	0.26	0.86	+0.03
	0.61	$e$	0.60	0.20	0.00	0.01	0.82	
	1.95	$e$	0.01	0.01	0.47	0.36	0.85	
$(V_{\text{Ga}}-V_{\text{P}})^0$	0.55	$a_1$	0.16	0.04	0.39	0.25	0.84	-0.02
	0.55	$e$	0.48	0.26	0.00	0.02	0.76	
	1.85	$e$	0.01	0.01	0.47	0.37	0.86	
$(V_{\text{Ga}}-V_{\text{P}})^{1+}$	0.52	$a_1$	0.22	0.09	0.27	0.20	0.78	-0.02
	0.52	$e$	0.39	0.30	0.00	0.03	0.73	
	1.73	$e$	0.01	0.02	0.47	0.37	0.87	
$(V_{\text{Ga}}-V_{\text{P}})^{2+}$	0.52	$a_1$	0.24	0.14	0.19	0.17	0.74	-0.04
	0.49	$e$	0.33	0.33	0.01	0.04	0.71	
	1.62	$e$	0.01	0.02	0.47	0.37	0.87	
$(V_{\text{Ga}}-V_{\text{P}})^{3+}$	0.47	$a_1$	0.22	0.14	0.19	0.17	0.73	-0.05
	0.39	$e$	0.30	0.33	0.01	0.04	0.68	
	1.56	$e$	0.01	0.02	0.47	0.37	0.87	
$(V_{\text{Ga}}-V_{\text{P}})^{4+}$	0.42	$a_1$	0.20	0.14	0.20	0.18	0.72	-0.06
	0.31	$e$	0.27	0.33	0.01	0.05	0.66	
	1.51	$e$	0.01	0.03	0.46	0.37	0.87	

three defect states of the divacancy located at the edges of the lower gap can well be viewed as being directly derived from the defect states of the corresponding isolated vacancies. Since these three defect states are not at all broken-bond-like, the interactions between them are expected to be very weak. Therefore, these defect states should be essentially monovacancylike, i.e., they should contain a large amount of the  $s$ -like character of either the three neighboring anion or the three neighboring cation atoms and have almost no contributions from the  $p$ -like orbitals of the neighboring atoms. This is just as we have found from the calculated localizations of the three defect states (not shown in Table I).

We have also done the calculations for the localizations of the fundamental gap-related defect states of the divacancies. We find that for each divacancy the two  $e$  fundamental gap states are localized mainly on either the neighboring atoms around the cation vacant site or the neighboring atoms around the anion vacant site, whereas the two  $a_1$  defect states at energies surrounding the lower edge of the fundamental band gap are localized on the neighboring atoms around both defect sites (see Tables II–IV). Furthermore, the wave functions of the two  $a_1$  defect states as well as the lower  $e$  gap state appear primarily as combinations of the  $p$ -like orbitals of the first-nearest-neighbor atoms. The wavefunction of the upper  $e$  gap state appears, however, primarily as a combination of both the  $s$ - and  $p$ -like orbitals of the first-nearest-neighbor atoms, with the sum of the localizations on the  $s$ -like orbitals larger than the sum of the localizations on the  $p$ -

like orbitals. Therefore, as one may expect, much of the localization character of the defect states of the isolated vacancies truly remains in the four fundamental gap-related defect states of the divacancy in GaP, GaAs, and GaSb. However, deviations in the localization character of the defect states from the monovacancies indeed appear. We find, for example, that the contributions of the three  $p$ -like orbitals on each neighboring atom of the divacancy to the fundamental gap-related defect states are no longer equal, and this deviation is especially significant for the two  $a_1$  and the lower  $e$  fundamental gap-related defect states.

In particular, we have found that for the neutral divacancies in the three Ga-related III-V compounds, the upper  $a_1$  and the lower  $e$  gap states are accidentally degenerate. We note that in this case we have assigned a fraction of an electron to each of the two states, because adding an electron to either of them causes its energy to move up higher than the other. We further note that the same cases have also been found in the present calculations for charge states of the divacancies in the three compounds (see Sec. III C), in a similar calculation for the divacancy in InP (Ref. 20) and in a local-density calculation for the divacancy in GaAs.<sup>19</sup>

### C. Charge states

We show in Figs. 2–4 our calculated energy levels of the fundamental gap states for the divacancies in GaP, GaAs, and GaSb at different charge states. The corre-

TABLE III. Same as Table II, but for the divacancy ( $V_{\text{Ga}} - V_{\text{As}}$ ) in GaAs.

Charge state	Energy level (eV)	Symmetry	$w_1^C$	$w_2^C$	$w_1^A$	$w_2^A$	$w^{cc}$	$Q^{cc}$ ( $e^-$ )
$(V_{\text{Ga}} - V_{\text{As}})^{3-}$	0.57	$a_1$	0.11	0.02	0.37	0.29	0.79	+0.06
	0.69	$e$	0.61	0.18	0.01	0.01	0.80	
	1.51	$e$	0.00	0.01	0.37	0.32	0.70	
$(V_{\text{Ga}} - V_{\text{As}})^{2-}$	0.41	$a_1$	0.17	0.02	0.35	0.25	0.79	+0.05
	0.65	$e$	0.60	0.18	0.01	0.01	0.80	
	1.42	$e$	0.01	0.01	0.40	0.33	0.75	
$(V_{\text{Ga}} - V_{\text{As}})^{1-}$	0.33	$a_1$	0.11	0.01	0.39	0.28	0.78	+0.03
	0.42	$e$	0.55	0.18	0.01	0.02	0.75	
	1.37	$e$	0.00	0.01	0.42	0.34	0.77	
$(V_{\text{Ga}} - V_{\text{As}})^0$	0.30	$a_1$	0.10	0.02	0.37	0.28	0.76	0.00
	0.30	$e$	0.45	0.21	0.01	0.03	0.69	
	1.34	$e$	0.00	0.01	0.42	0.35	0.79	
$(V_{\text{Ga}} - V_{\text{As}})^{1+}$	0.25	$a_1$	0.11	0.03	0.32	0.26	0.73	-0.01
	0.25	$e$	0.38	0.23	0.01	0.03	0.65	
	1.26	$e$	0.01	0.01	0.43	0.36	0.80	
$(V_{\text{Ga}} - V_{\text{As}})^{2+}$	0.20	$a_1$	0.13	0.05	0.27	0.24	0.68	-0.01
	0.20	$e$	0.33	0.24	0.01	0.04	0.62	
	1.17	$e$	0.01	0.01	0.43	0.37	0.82	
$(V_{\text{Ga}} - V_{\text{As}})^{3+}$	0.17	$a_1$	0.15	0.07	0.21	0.21	0.63	-0.03
	0.17	$e$	0.30	0.25	0.01	0.04	0.60	
	1.08	$e$	0.01	0.01	0.43	0.37	0.82	
$(V_{\text{Ga}} - V_{\text{As}})^{4+}$	0.16	$a_1$	0.15	0.08	0.18	0.19	0.60	-0.06
	0.13	$e$	0.26	0.25	0.01	0.05	0.57	
	1.01	$e$	0.01	0.01	0.42	0.38	0.82	

TABLE IV. Same as Table II, but for the divacancy ( $V_{Ga} - V_{Sb}$ ) in GaSb.

Charge state	Energy level (eV)	Symmetry	$w_1^C$	$w_2^C$	$w_1^A$	$w_2^A$	$w^{ec}$	$Q^{ec}$ ( $e^-$ )
$(V_{Ga} - V_{Sb})^{2-}$	0.24	$a_1$	0.18	0.05	0.18	0.20	0.61	+0.02
	0.36	$e$	0.43	0.19	0.01	0.03	0.66	
$(V_{Ga} - V_{Sb})^{1-}$	0.19	$a_1$	0.15	0.04	0.18	0.21	0.57	0.00
	0.24	$e$	0.38	0.20	0.01	0.04	0.62	
	0.84	$e$	0.00	0.01	0.34	0.32	0.67	
$(V_{Ga} - V_{Sb})^0$	0.17	$a_1$	0.14	0.06	0.16	0.21	0.57	0.00
	0.17	$e$	0.32	0.21	0.01	0.04	0.58	
	0.81	$e$	0.00	0.01	0.35	0.33	0.69	
$(V_{Ga} - V_{Sb})^{1+}$	0.20	$a_1$	0.16	0.09	0.11	0.16	0.52	-0.04
	0.19	$e$	0.28	0.22	0.02	0.05	0.57	
	0.72	$e$	0.01	0.01	0.35	0.34	0.70	
$(V_{Ga} - V_{Sb})^{2+}$	0.17	$a_1$	0.15	0.09	0.10	0.17	0.50	-0.05
	0.13	$e$	0.26	0.22	0.01	0.05	0.54	
	0.69	$e$	0.01	0.01	0.35	0.35	0.71	
$(V_{Ga} - V_{Sb})^{3+}$	0.15	$a_1$	0.14	0.08	0.10	0.17	0.49	-0.06
	0.08	$e$	0.23	0.21	0.01	0.05	0.50	
	0.67	$e$	0.01	0.01	0.35	0.35	0.72	
$(V_{Ga} - V_{Sb})^{4+}$	0.14	$a_1$	0.13	0.08	0.10	0.17	0.48	-0.06
	0.05	$e$	0.20	0.19	0.01	0.05	0.46	
	0.65	$e$	0.01	0.01	0.35	0.35	0.73	

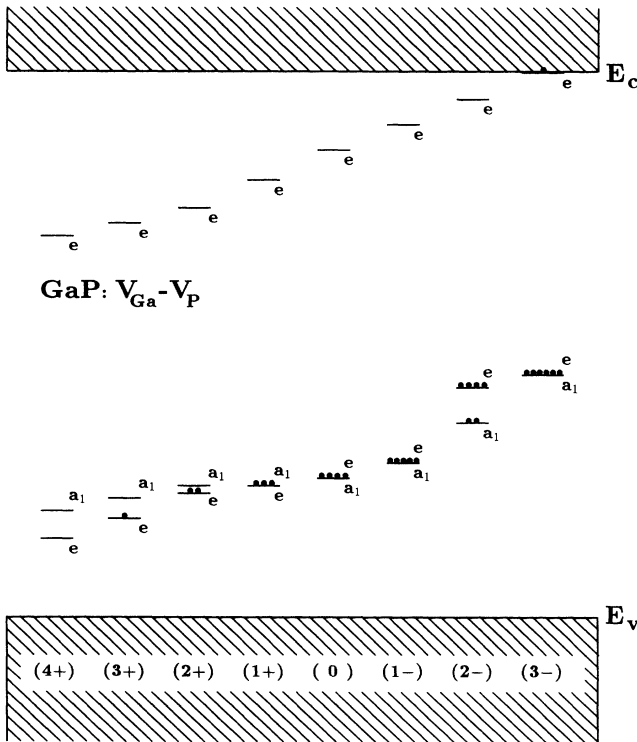


FIG. 2. Calculated defect-induced energy levels in the fundamental band gap for the undistorted divacancy at different charge states in GaP. The symbols given in the parentheses indicate the charge states of the divacancy defect.  $E_v$  and  $E_c$  denote the edges of the valence band and the conduction band, respectively. Solid circles indicate the occupancy of the defect levels. The symmetry properties of the defect levels are given in the figure.

sponding values of these energy levels are given in Tables II–IV together with their localizations and the net charges accumulated in the defect extended central cell (defined as a divacancy plus its six first- and eighteen

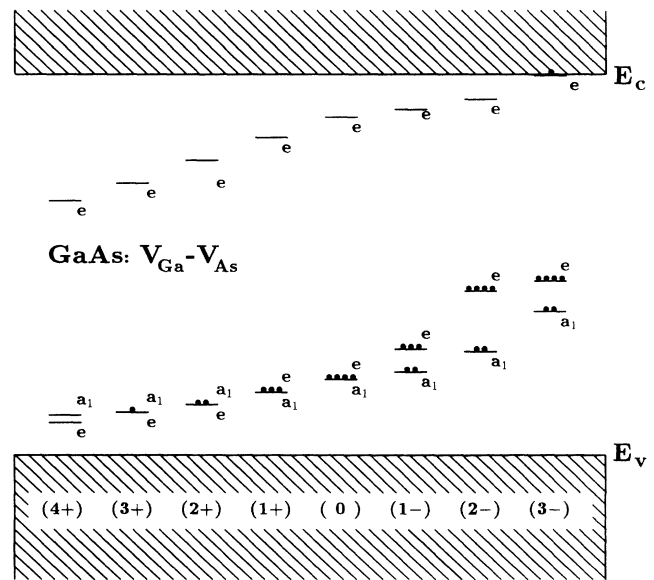


FIG. 3. Calculated defect-induced energy levels in the fundamental band gap for the undistorted divacancy at different charge states in GaAs. The symbols given in the parentheses indicate the charge states of the divacancy defect.  $E_v$  and  $E_c$  denote the edges of the valence band and the conduction band, respectively. Solid circles indicate the occupancy of the defect levels. The symmetry properties of the defect levels are given in the figure.

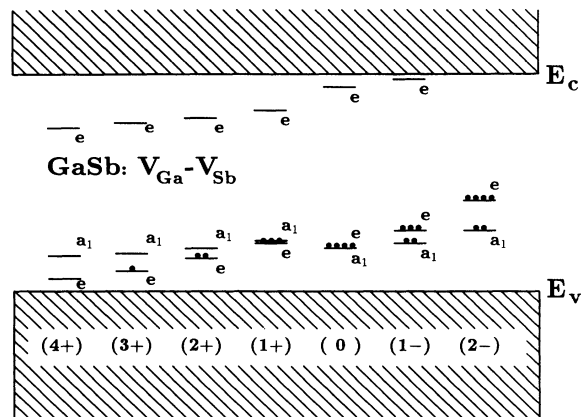


FIG. 4. Calculated defect-induced energy levels in the fundamental band gap for the undistorted divacancy at different charge states in GaSb. The symbols given in the parentheses indicate the charge states of the divacancy defect.  $E_v$  and  $E_c$  denote the edges of the valence band and the conduction band, respectively. Solid circles indicate the occupancy of the defect levels. The symmetry properties of the defect levels are given in the figure.

second-nearest-neighbor atoms). Here we have not shown the results of our calculations for the lower  $a_1$  fundamental gap-related levels of the divacancies in the three compounds, because they are found to be fully occupied by two electrons at all the predicted charge states and to be located at energies just below or above the top of the valence band. Thus, no matter what charge state it is, a divacancy in the three compounds are always found to give two  $a_1$  and two  $e$  defect levels in and around the fundamental band gap, as we expected in Fig. 1. It has been clearly shown in Figs. 2–4 that for each divacancy the upper  $a_1$  and the lower  $e$  fundamental gap levels are located at close energies in the lower half of the fundamental band gap and have an energy ordering that is dependent on the defect charge state. We believe that this is a typical nature of the electronic structure of divacancies in many III-V compound semiconductors and makes the experimental identification of these defects difficult.

Tables II–IV show that for the divacancies in GaP, GaAs, and GaSb the two  $e$  fundamental gap states are basically monovacancylike states, namely the upper (lower)  $e$  gap state is mainly localized on the first- and the second-nearest-neighbor atoms around the anion (cation) vacant site and has little contributions from the first- and second-nearest-neighbor atoms around the cation (anion) vacant site. The tables also show that the  $a_1$  fundamental gap state contains significant contributions from both the first- and the second-nearest-neighbor atoms around the anion vacant site and those around the cation vacant site. This is also true for the lower  $a_1$  fundamental gap-related defect state (not shown in these tables). Here we do not mean that the contributions to the two  $a_1$  states from the two groups of neighboring atoms are equal. Actually, the upper (lower)  $a_1$  state is found to have a localization on

the neighboring atoms around the anion vacant site larger than that on the neighboring atoms around the cation vacant site. All these results are just as we expect from our molecular-orbital model presented in Fig. 1. Tables II–IV also show that the defect gap levels are very localized for the divacancy in GaP and become less localizations for the divacancy in GaSb. In between are the localizations of the corresponding gap levels of the divacancy in GaAs. In these tables, we have not given the calculated values for the localizations of the four fundamental gap-related defect states on the individual atomiclike orbitals. We would like to note here that for the divacancy at charge states the upper  $a_1$  and the lower  $e$  gap states always have roughly equal contributions from the  $p$ -like orbitals of the three first-nearest-neighbor atoms of the anion vacant site and significantly different contributions from the  $p$ -like orbitals of the three first-nearest-neighbor atoms of the cation vacant site, and that a large contribution to the upper  $e$  gap state always comes from the  $s$ -like orbitals of the three first-nearest-neighbor atoms around the anion vacant site.

A remarkable result of our calculations is that the divacancies in the three III-V compound semiconductors can have many different charge states and the upper  $a_1$  and the lower  $e$  fundamental gap levels correlate strongly, giving the feature that the energy positions of these two defect levels are not very sensitive to the change in the charge states. This result was also found for the divacancy in InP.<sup>20</sup> The only difference is that in that case the  $a_1$  and  $e$  levels were found to be located around the middle of the fundamental band gap, while here the two corresponding levels are found to be located below the middle of the fundamental band gap. The physical origin of this electronic property was explained in detail in Ref. 20 and will not be repeated here. We just stress that nonequivalent  $p$ -like orbitals of a first-nearest-neighbor atom of the cation vacant site make quite different contributions to the gap levels and, thus, if the self-interactions are eliminated, the intra-atomic electron-electron interactions acting on the  $p$ -like orbitals should vary unequally with the occupancy of the gap levels. For a  $p$ -like orbital of an atom on which a gap level is more localized, the increase in the energy of the orbital due to adding electrons to the gap level is less than that for a  $p$ -like orbital of that atom on which the gap level is less localized. When self-consistency is reached, the energy of the  $p$ -like orbital on which the gap level is more localized may turn out to decrease with an increase in the number of electrons on the gap level. Therefore, for the defect gap levels, such as the upper  $a_1$  and the lower  $e$  gap levels, being very much localized on the three first-nearest-neighbor anion atoms and having quite different localizations on the nonequivalent orbitals of each of the neighboring anion atoms, an increase in their electron occupancy will result in only a small increase or even a decrease in the energies of the defect levels. Here, we note again that for those charge states at which the lower  $e$  and upper  $a_1$  gap levels of the divacancies are actually degenerate, fractions of electrons have been assigned to the two levels.

In order to justify the neglect of longer-ranged contributions to the defect potential in our calculations, we

have given in Tables II–IV the calculated net charges accumulated in the extended central cell of the divacancy defects. It can be seen that they are rather small, on the order of between  $-0.06$  and  $+0.06$  electron charge ( $e^-$ ) for all the calculated charge states of the defects. In the present calculations, the contributions from interatomic and intra-atomic electron-electron interactions to the self-consistent potentials on all the atoms in the extended central cell of the defects have been taken into account. We therefore believe that the inclusion of contributions to the defect potential from any longer-ranged interatomic electron-electron interactions and the intra-atomic electron-electron interactions in the atoms outside the extended central cell should not result in any significant changes in the above-calculated electronic structures.

Lattice distortions can of course change the electronic structure of the divacancies in the three Ga-related compounds. For instance, an  $e$  level will split into two levels by a Jahn-Teller distortion. However, we strongly suspect that the lattice distortions for the divacancy defects at all the charge states we have calculated, except the triple-negative charge state, are small in magnitude. Such consideration is reasonable because, in recent self-consistent calculations for the isolated vacancies in GaAs using local-density approximation, Laasonen, Nieminen, and Puska<sup>32</sup> found that the lattice distortions are rather small for the isolated Ga vacancy at the neutral and negative charge states and for the isolated As vacancy at the neutral and positive charge states, and also because that at most of the studied charge states the divacancies in the three Ga-related compounds can be thought of as first-nearest-neighbor complex pairs of negatively charged cation vacancy and positively charged anion vacancy. In the exceptional case where the divacancies are at the triple-negative charge state and the upper  $e$  gap level is occupied by an electron, large lattice distortions may occur. This is because the upper  $e$  gap level is found to be an anion monovacancy  $t_2$ -like state, and because strong lattice relaxations were found to occur for the anion vacancy at negative charge states in GaAs.<sup>32</sup> The lattice distortions due to the occupations of the upper  $e$  gap level by electrons will split the level into two levels with an occupied level being lowered more deeply into the fundamental gap and the other one possibly being pushed up to the conduction band. Thus the triple- and possibly also the quadruple-negative charge states may indeed be observable defect states for the divacancies in GaP, GaAs, and GaSb.

#### D. Comparison to literature

For the divacancy in III-V compound semiconductors, little is known experimentally. In a review of the studies of the irradiation-induced defects in GaAs by deep-level transient spectroscopy,<sup>30</sup> the divacancy defects were assumed to be produced by electron irradiation in  $n$ -type GaAs and annealed below room temperature. In a very recent study based on an analysis of thermodynamic data on the native defect  $EL2$  in GaAs, Morrow<sup>18</sup> showed that the divacancy is one important primary defect in melt-grown and epitaxially grown GaAs. However, no

definite energy positions of the defect levels associated with the divacancy were reported in these two works, thus comparisons of the present calculations with them cannot be done. In two studies of the defects in GaAs by the positron-annihilation technique,<sup>6,7</sup> the divacancy defects were described as being responsible for the positron trapping with an increase in the positron lifetime from the bulk value. In these studies, the authors claimed that they find the positron trapping by the divacancies in  $n$ -type,  $p$ -type, and semi-insulating GaAs materials. The very weak point of the assignment of Refs. 6 and 7 is that in  $p$ -type GaAs the divacancy is predicted by the present calculations to be at highly positive charge states and thus becomes a less effective positron trap. It is worthwhile to note that in another positron-annihilation study of the vacancy defects in GaAs,<sup>8</sup> this increase in the positron lifetime was assumed to be due to the positron trapping by the arsenic vacancy at the single-negative charge state ( $V_{As}^{1-}$ ). We have not found any relevant experimental studies for the divacancies in GaP and GaSb.

We are not aware of any theoretical calculations for the electronic structure of the divacancies in the Ga-related III-V compound semiconductors other than the non-self-consistent tight-binding calculations of Reinecke<sup>21</sup> and the local-density calculations of Baraff and Schlüter.<sup>19</sup> Reinecke found that there are four fundamental gap levels, two  $a_1$  and two  $e$  defect levels, associated with the divacancy in GaP and GaAs, qualitatively consistent with our model presented in Fig. 1. However, in his calculations the effect of the charge transfer between the upper  $a_1$  and lower  $e$  gap levels were fully eliminated. This effect is very crucial in the calculations for the divacancies in III-V compound semiconductors, because, for example, for the divacancies at the neutral charge state the calculations without taking the effect of the charge transfer into account will result in an unstable electronic configuration, that is, the fully occupied upper  $a_1$  gap level stays at an energy higher than the partially occupied lower  $e$  gap level. In the local-density calculations Baraff and Schlüter predicted that the divacancy in GaAs introduces an  $a_1$  and an  $e$  defect state, with the same positions of energy, into the fundamental band gap. We believe that the two states correspond to the upper  $a_1$  and lower  $e$  fundamental gap levels of our calculations. However, no other gap state was found in the local-density calculations, in contrast to our calculations where another  $e$  level is found to be located just below the bottom of the conduction band. A big disagreement between our calculations and the local-density calculations is as follows: We have found that the energy positions of the upper  $a_1$  and lower  $e$  gap levels are not very sensitive to the charge states of the defect (e.g., the energy positions of the two gap levels are shifted by about 0.05 eV per bound electron when going from the triple-positive to the neutral charge state), while Baraff and Schlüter found that the energy positions of the two corresponding gap states are changed by about 0.2 eV per bound electron with the charge state of the defect. We believe that this disagreement is mainly due to whether or not the self-interactions are eliminated from the self-consistent poten-



tials. There is no doubt that up-to-date local-density calculations are the most reliable methods for the study of the isolated point defects or impurities in semiconductors. However, the reliability of the methods might be reduced in the study of the defect complexes by reason that the defect potential of the complexes become significantly anisotropic in general (i.e., their symmetries are usually reduced). In a self-interaction-corrected local-density calculation for the interstitial transition-metal impurities in silicon,<sup>33</sup> Zunger found that the self-interaction correction reduces the crystal-field splittings (the energy differences between  $e$  and  $t_2$  gap levels) of the impurities by several tenths of an eV. He concluded that a full-potential local-density model alone is insufficient to describe the correct many-electron ground states of interstitial impurities. Our present calculations suggest that the inclusion of the self-interaction correction in local-density calculations may also significantly reduce charge splittings of the gap levels of defect complexes.

#### IV. SUMMARY

In this paper, we reported on self-consistent semi-empirical tight-binding calculations for the electronic structure of the undistorted divacancies in GaP, GaAs, and GaSb. The calculations are done with the use of the recursion method (a real Green's-function method) and the supercell approximation. The general characteristics of the electronic structure of the divacancies has been discussed. We have first presented and discussed the results of the calculations for divacancies at the neutral charge state. We show that each divacancy can basically introduce seven defect levels: Two  $a_1$  defect levels and one  $e$  defect level are located at energies close to the edges of the lower gap, and the other four defect levels, two  $a_1$  and two  $e$  defect levels, are located at energies in and around the fundamental band gap. A simple model for the description of the physical origin of these four fundamental gap-related defect levels is given. We have found that for the divacancy at the neutral charge state the upper  $a_1$  and the lower  $e$  defect levels are accidentally degenerate, stay in the lower half of the fundamental band gap, and have very different localization properties.

We have also done calculations for charged divacancies in GaP, GaAs, and GaSb. The results of our calculations

show that a divacancy in the three compounds can have many different charge states. The upper  $a_1$  and the lower  $e$  fundamental gap-related defect levels are located in the lower half of the fundamental gap at all the predicted charge states and stay at close energies. In particular, we have found that the two fundamental gap levels correlate strongly over a range of charge states, giving the feature that their energy positions are not very sensitive to the change of the charge states of the defect in this range. We believe that this feature is a fundamental property of the electronic structure of divacancies in many III-V compound semiconductors. We have argued that the intra-atomic electron-electron interactions take the major responsibility for the insensitivity of the upper  $a_1$  and lower  $e$  gap levels of the divacancies to the defect charge state.

We have compared our results with experiments, particularly with positron-annihilation experiments. We have found that in  $p$ -type GaAs the divacancy should stay at a highly positive charge state. The assignment of the positron trapping with an increase in the positron lifetime from the bulk value to the divacancy in GaAs has therefore been questioned. We have also made a critical comparison with other theoretical calculations for the divacancies. We point out that non-self-consistent calculations may not give correct predictions of the ordering of the defect gap levels. We have shown that both the local-density calculations and the present calculations predict that the upper  $a_1$  and lower  $e$  gap levels of the divacancy in GaAs stay at very close energies. We have also shown the difference between the local-density calculations and the present calculations in the dependence of the energy positions of the two gap levels on the charge state of the divacancy in GaAs. We argue that the occurrence of this difference is due to whether or not the self-interactions are eliminated from the self-consistent potentials. The self-interactions are nonphysical and have been well eliminated in this work.

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