

Chemical trends for native defects in III-V—compound semiconductors

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We present energy levels calculated for both vacancies and antisite defects in nine different III-V compounds. It is shown that the chemical trends for the neutral, unrelaxed vacancy levels as obtained with more sophisticated linear combination of atomic orbital models can be reproduced and extrapolated by use of a simple, rescaled defect-molecule model. The only input parameters needed are the hybrid orbital energies of the nearest-neighbor atoms and the phototreshold energies of the host materials. We also use this model to calculate trends for the antisite-induced energy levels which are consistent with experiments on P_{Ga} and As_{Ga} . Cation antisite defects are predicted to produce deep levels within the main energy gap for most of the compounds investigated. Furthermore, the trends for cation antisite defect levels are in striking quantitative agreement with the observed, characteristic Fermi-level pinning energies at Schottky barriers on both *n*- and *p*-type materials. Therefore, our calculations support the native-defect model proposed by Spicer *et al.*, but with a single defect in different charge states mainly responsible for the observed pinning energies.

I. INTRODUCTION

In the last decade, native defects in semiconductors have been extensively studied because they are believed to produce deep trap levels which may have significant influence on device performance. Especially the antisite defects in III-V compounds have found considerable attention because they seem to be the thermodynamically most probable native point defects.^{1,2} In fact, the most important deep donor EL2 in GaAs has been rather safely identified as the As_{Ga} antisite defect.³ The importance of native defects has been further stressed by the experimental observation that they seem to cause the characteristic Fermi-level pinning energies (FLPE) at Schottky barriers and semiconductor interfaces.^{4,5} Several different candidates, among them the antisite defects, have been proposed.⁵⁻⁷ Experimental results have also indicated that a single defect or defect complex alone could be responsible for the observed FLPE in both *n*- and *p*-type materials.⁸

These findings make it interesting to study the chemical trends of antisite defects in different charge states and compare them to the trends for measured FLPE in III-V compounds. A further reason to study *chemical trends* is that the defect problem is so involved that up to now no one has succeeded in calculating defect levels accurately enough to identify measured levels directly.⁹

Chemical trends for both vacancies and antisite defect levels have been obtained using the semiempirical tight-binding (TB) method.¹⁰⁻¹³ These calculations have the shortcoming that they do not include different charge states of the defects, which should be important for antisite defects because they can be expected to form double acceptors and double donors. A simple model recently presented for chemical trends of antisite defects in different charge states has the disadvantage that it needs considerable experimental input data so that its practical applicability is limited to only a few compounds.¹⁴

Here, we first use a rescaled defect-molecule model to calculate the trends of energy levels produced by neutral, unrelaxed vacancies in III-V compounds. As will be shown later, those levels are needed to calculate antisite defect levels within the same model. The rescaled defect-molecule model calculations and the results will be presented in Sec. II. In Sec. III we briefly discuss antisite defects as a possible origin of the observed, characteristic FLPE.

II. NATIVE-DEFECT LEVELS WITHIN A RESCALED DEFECT-MOLECULE MODEL

The defect-molecule model (DMM) has been frequently used to give insight into the basic physical processes involved with the formation of point defects in semiconductors.¹⁵⁻¹⁷ It is based on the molecular model of a covalent solid where all the atoms are assumed to be coupled only to their nearest-neighbor atoms and only via sp^3 hybrids directed toward each other.¹⁵ Therefore, the energy levels of the host are those of a two-atom molecule consisting of two neighboring host atoms, whereas the levels introduced by a substitutional point defect are described by a two-atom molecule consisting of the defect atom and one of its nearest-neighbor host atoms. Each of these atoms is characterized by its (atomic) hybrid energy ϵ_h . Consequently, the two energy levels ϵ^b and ϵ^a (bonding and antibonding) are simply given by

$$\epsilon^a = \frac{\epsilon_h^{NN} + \epsilon_h^d}{2} \mp \left[\frac{(\epsilon_h^{NN} - \epsilon_h^d)^2}{4} + (V_2^h)^2 \right]^{1/2}. \quad (1)$$

ϵ_h^{NN} and ϵ_h^d are the hybrid orbital energies of the nearest neighbor (NN) and defect atom (*d*), respectively. V_2^h is called the hybrid covalent energy and represents the interatomic matrix element which couples the two atoms via their hybrid orbitals lying on the bond axis.¹⁸ Both ϵ^a and ϵ^b are fourfold degenerate within this simple model.

Taking into account more coupling terms, however, splits each of these levels into a nondegenerate A_1 and a threefold degenerate T_2 level.¹⁵

This model exhibits a special property which is characteristic of all TB models.¹⁶ If ϵ_h^d approaches plus (minus) infinity the bonding (antibonding) level approaches ϵ_h^{NN} whereas the antibonding (bonding) level follows ϵ_h^d to plus (minus) infinity. Therefore, ϵ_h^{NN} represents a hostlike "pinning" level for (very) deep levels within this model. Using atomic orbital energies to obtain the hybrid orbital energies ϵ_h^{NN} and ϵ_h^d and V_2^h known from the semiempirical TB method, it is possible to understand the formation of deep defect levels qualitatively, whereas the DMM has turned out to be too crude to be quantitative.¹⁵ Here we present a semiempirical rescaled defect-molecule model which, however, is in quantitative agreement with previous TB calculations for vacancy levels. We further apply this model to antisite defects and include charge-state effects qualitatively.

A. Neutral, unrelaxed vacancies

According to the brief introduction, a single vacancy is described by a defect molecule where one of the two host atoms has been removed. Therefore, within the DMM the energy levels introduced by a vacancy are given by the fourfold-degenerate energy level ϵ_h^{NN} which splits up into an A_1 and a threefold-degenerate T_2 level when interactions beyond the DMM are included.¹⁵ For the nearest-neighbor atom, $|\epsilon_h^{NN}|$ also represents the ionization energy to remove an electron from the hybrid orbital. Inspired by the finding that the top of the valence band $|E_v|$, as obtained by atomic orbital energies within the semiempirical TB method, is in a simple linear relationship with the photothreshold energy Φ of the semiconductor, one may also suspect that the energy $|\epsilon_h^{NN}|$ is a measure for the ionization energy E_I of an electron bound to the vacancy.¹⁸ We therefore write

$$E_I = \Phi - \epsilon_v, \quad (2)$$

where ϵ_v is a vacancy level of A_1 or T_2 symmetry relative to the valence-band edge E_v .

TABLE I. The used values for the photothreshold Φ (Refs. 18, 20, and 21) and the atomic hybrid energies ϵ_h^{NN} (Ref. 22).

Material	Φ (eV)	Nearest-neighbor atom	ϵ_h^{NN} (eV)
AlP	6.02	Al	7.15
AlAs	5.65	Ga	7.25
AlSb	5.27	In	6.84
GaP	6.00	P	11.91
GaAs	5.47	As	11.61
GaSb	5.00	Sb	10.23
InP	5.69		
InAs	5.31		
InSb	4.77		

Substituting calculated values¹⁰⁻¹³ for the same vacancy state in different III-V compounds into (2) and using experimental values for Φ , one finds that (2) yields ionization energies which are proportional to $|\epsilon_h^{NN}|$, i.e.,

$$E_I = \alpha |\epsilon_h^{NN}|, \quad (3)$$

with one parameter α for a given vacancy state in all III-V compounds.¹⁹ The values used for Φ and the hybrid energies ϵ_h^{NN} are given in Table I. Since it is known that Φ depends on the surface we use values measured at the (110) surface.^{20,21}

In Tables II and III, it is shown that this rescaled DMM can reproduce the chemical trends of vacancy levels as obtained by more elaborate TB calculations within the accuracy of these calculations.²³ Furthermore, we can extrapolate this model to AlSb, GaSb, and InSb using (2) and (3) combined to

$$\epsilon_v = \Phi - \alpha |\epsilon_h^{NN}|. \quad (4)$$

Table II shows our results for the cation vacancy-induced A_1 and T_2 levels compared to previous TB calculations. The A_1 levels are always obtained in the valence band, whereas the T_2 levels lie close to the valence-band edge. Table II further exhibits that our values and trends are in good agreement with previous TB calculations and that they usually resemble the results of Refs. 12 and 13

TABLE II. Calculated cation vacancy levels relative to the valence-band edge compared to previous TB calculations. E_g is the main energy gap and α is the rescaling factor of (3).

	E_g (eV)	A_1 (eV)	T_2 (eV)	A_1^a (eV)	T_2^a (eV)	A_1^b (eV)	T_2^b (eV)
α		0.53	0.47				
AlP	2.52	-0.34	0.42	<0	0.32		
AlAs	2.23	-0.55	0.19	<0	0.17	-0.60	0.81
AlSb	1.69	-0.19	0.46				
GaP	2.35	-0.36	0.40	<0	0.07	-0.55	0.44
GaAs	1.52	-0.73	0.01	<0	-0.03	-0.74	0.44
GaSb	0.81	-0.46	0.19				
InP	1.42	-0.67	0.09	<0	<0	-0.55	0.44
InAs	0.42	-0.89	-0.15	<0	<0	-0.54	0.27
InSb	0.24	-0.69	-0.04				

^aValues taken from the figures in Refs. 12 and 13.

^bValues taken from Refs. 10 and 11.

TABLE III. Calculated anion vacancy levels relative to the valence-band edge compared to previous TB calculations. E_g is the main energy gap and α is the rescaling factor of (3).

	E_g (eV)	A_1 (eV)	T_2 (eV)	A_1^a (eV)	T_2^a (eV)	A_1^b (eV)	T_2^b (eV)
α		0.68	0.55				
AlP	2.52	1.19	2.08	0.94	2.22		
AlAs	2.23	0.82	1.71	0.82	1.99	0.77	1.58
AlSb	1.69	0.44	1.33				
GaP	2.35	1.10	2.00	1.10	2.07	0.38	1.38
GaAs	1.52	0.57	1.47	0.61	1.46	0.34	1.20
GaSb	0.81	0.10	1.00				
InP	1.42	1.07	1.91	1.65	1.80	0.76	> 1.35
InAs	0.42	0.69	1.53	1.15	1.20	> 0.36	> 0.36
InSb	0.24	0.15	0.99				

^aTaken from the figures of Refs. 12 and 13.

^bTaken from Refs. 10 and 11.

more closely than those from Lin-Chung and Reinecke.^{10,11}

Our results for the anion vacancy levels given in Table III predict that the A_1 level usually lies within the main gap (except for InAs where it is found in the conduction band). The T_2 levels are also found to lie in the main energy gap for all indirect-gap compounds investigated and in the conduction band for all direct-gap compounds. Again, our results are closer to those given in Refs. 12 and 13 than those given by Lin-Chung *et al.*¹⁰ and Reinecke.¹¹

Except for the extreme simplicity of the underlying model, uncertainties in Φ (about 0.2 eV) and in the atomic orbital energies limit the accuracy of this model. Also, every reasonable theory for vacancy levels should include lattice relaxation as well as charge state effects in a self-consistent way.⁹ Here, we are only interested in the neutral, unrelaxed vacancy levels because these are needed to calculate antisite defect levels within the rescaled DMM.

B. Antisite defects

Within the defect-molecule model, the energy levels introduced by an isolated antisite defect are equivalent to those of a diatomic molecule consisting of two cations [cation-on-anion antisite defect (CAS)] or two anions [anion-on-cation antisite defect (AAS)]. Therefore, with $\epsilon_h = \epsilon_h^{\text{NN}} = \epsilon_n^d$, (1) reduces to

$$\epsilon^a = \epsilon_h \mp |U|, \quad (5)$$

where ϵ_h is the cation or anion hybrid energy and U is the interatomic matrix element coupling the two identical atoms. However, within the DMM, ϵ_h also represents the vacancy level for the same lattice site relative to the vacuum. If we apply the rescaled DMM, we have to replace ϵ_h by $\alpha\epsilon_h$ and (referring energies to the valence-band edge) we obtain

$$\epsilon^a = \epsilon_h \mp |U|, \quad (5')$$

with ϵ_h from (4) or Tables II and III.

The CAS defect produces a repulsive defect potential for electrons because the cation is less electronegative than the anion. Therefore, one can expect that a T_2 level is pushed out of the valence band and pins against a higher T_2 vacancy level. Similarly, the AAS defect produces an attractive defect potential for electrons and so an A_1 state will be pulled down from the conduction band and pin against a lower-lying A_1 vacancy level. This can be qualitatively understood with the DMM.^{15,16} Additional defect levels may occur in the gap. Within the DMM the AAS defect could pull down a T_2 level from the conduction band, the CAS defect might push up an A_1 level from the valence band. A simple estimate using the DMM shows that the latter is very unlikely, whereas the former case may actually occur. A recent experiment indicates the existence of T_2 levels (slightly) above the conduction-band edge for As_{Ga} .²⁴ However, further information about those levels seems to be necessary before the applicability of the DMM to these levels can be decided. Therefore, we confine our attention to the corresponding A_1 state for the AAS defect and the T_2 state for the CAS defect. We have to use the values obtained for the A_1 cation vacancy levels and the T_2 anion vacancy levels for ϵ_h in (5') for the anion and cation antisite defects, respectively.

In order to position the antisite defect levels relative to the valence band, we adapt the interatomic matrix element U to experimental results in a single material. As cation and anion antisite defects are expected to represent double acceptors and double donors, respectively, this has to be done for each different charge state. To obtain the chemical trends for antisite defects we write down,

$$U = \beta d^{-2}, \quad (6)$$

i.e., we assume that U scales with the bond length d in the same way as the hybrid covalent energy V_2^h of (1). Such a scaling rule with d^{-2} for V_2^h has been found valid in the semiempirical TB method for perfect semiconductors.¹⁸

Therefore, the basic assumptions in (5) are that such a scaling law also holds for the cation-cation and anion-anion bond, that the inclusion of charge state effects into U does not influence this rule significantly, and that no essential lattice relaxation around the defect occurs. As antisite defects form deep impurities, i.e., the short-range part of the defect potential dominates the Coulomb part, the second assumption seems to be justified. ESR measurements show that P_{Ga} and As_{Ga} maintain the T_d symmetry in their neighborhood so that only a change in the bond length d around the defect may occur.^{25,26} This effect can be, at least partially, included in the parameter β . The values of β for the different charge states of the A_1 levels and the T_2 levels of the AAS and CAS defect, respectively, are determined by requiring them to reproduce the experimental results for antisite levels in a single compound (e.g., GaAs) via (5') and (6).

The only rather well identified antisite levels are those of As_{Ga} and P_{Ga} , whereas no safe identification of any cation antisite level (or even any CAS defect itself) has been reported up to now.^{3,27} For As_{Ga} , the two ionization energies have been reported to be $\epsilon(0|+) = E_v + 0.75$ eV and $\epsilon(+|++) = E_v + 0.52$ eV.³

A simple linear interpolation leads to the approximate energy levels at 0.41, 0.64, and 0.87 eV for As_{Ga} in the doubly- and singly-ionized and neutral charge state, respectively.^{14,28} Due to the lack of equivalent experimental data about Ga_{As} one can only use chemical trends to estimate the position of the corresponding energy levels. As Ga_{As} should act as a double acceptor, chemical trends for experimental ground-state energies of single acceptors as a function of atomic p energies may be used.¹⁶ With this method one would estimate the single- and double-negative levels in the lower and middle part of the main energy gap.

Indeed, two native hole traps, commonly named A and B , are reasonable candidates as Ga_{As} defect levels.^{29,30} They have been found to be simultaneously present in almost all liquid-phase-epitaxial grown GaAs samples. Their thermal activation energies are approximately $E_v + 0.40$ eV and $E_v + 0.71$ eV. Following Schneider,³¹

we tentatively assume that A and B are the two ionization energies for the T_2 levels of Ga_{As} . The estimated energies for the neutral, single-, and double-negative charge state are 0.25, 0.55, and 0.85 eV.^{14,28} With these values as input data and the model described above we obtain the desired energy levels of the antisite defects as presented in Table IV.

In general, AAS defects are predicted to produce deep A_1 levels within the main energy gap. Positioning the As_{Ga} levels according to experiment gives the A_1 levels for P_{Ga} as 1.36, 1.12, and 0.87 eV above the valence-band edge. These values are in good agreement with the experimental values for the two ionization energies $\epsilon(+|++) = E_c - 1.1$ eV and $\epsilon(0|+) \geq E_c - 0.8$ eV compared to $\epsilon(+|++) \cong E_c - 1.35$ eV and $\epsilon(0|+) \cong E_c - 1.1$ eV with our model.²⁷

Our trends for the A_1 levels of the AAS defects compare well with previous TB calculations. The levels obtained by Lin-Chung *et al.*¹⁰ and Reinecke¹¹ lie consistently higher (~ 0.3 – 0.4 eV), those of Ho and Dow¹² and Buisson and co-workers³² lie consistently lower (~ 0.2 eV) than our levels A_1^0 in Table IV.

If we position the levels for Ga_{As} according to the experimental values for the deep acceptor levels A and B as described before, we obtain the values given in Table IV. Also the acceptorlike T_2 levels produced by CAS defects are generally predicted to lie deep in the main energy gap. Only for In_{As} and In_{Sb} are the charged T_2 states (T_2^- and T_2^{--}) predicted to lie within the conduction band. This is especially pronounced in the case of In_{As} where T_2^{--} and T_2^- are predicted to lie about 0.6 and 0.3 eV above the conduction-band edge, respectively. Previous TB calculations show the same chemical trends for T_2 CAS defect levels. However, their absolute position is about 0.6 eV lower than for our results and are therefore generally obtained in the valence band.^{12,32} As that model also predicts the T_2 states of single acceptors on the anion site systematically to be too low, we believe that this may also be the case for the cation-on-anion double acceptors.¹⁶ Agreement with a previously suggested model concerning chemical trends is good.¹⁴

TABLE IV. A_1 levels for the anion and the T_2 levels for the cation antisite defects in different charge states ν relative to the valence-band edge. The interatomic matrix elements U^ν for the charge state ν are also given. E_g is the main energy gap.

	E_g (eV)	Anion antisite defect						Cation antisite defect					
		U^0 (eV)	U^+ (eV)	U^{++} (eV)	A_1^0 (eV)	A_1^+ (eV)	A_1^{++} (eV)	U^0 (eV)	U^- (eV)	U^{--} (eV)	T_2^0 (eV)	T_2^- (eV)	T_2^{--} (eV)
AIP	2.52	1.72	1.48	1.23	1.38	1.14	0.89	1.31	0.99	0.67	0.77	1.09	1.41
AlAs	2.23	1.63	1.39	1.16	1.08	0.84	0.61	1.24	0.94	0.63	0.47	0.77	1.08
AlSb	1.69	1.36	1.16	0.97	1.17	0.97	0.78	1.03	0.78	0.53	0.30	0.55	0.80
GaP	2.35	1.72	1.48	1.23	1.36	1.12	0.87	1.31	0.99	0.67	0.69	1.01	1.33
GaAs ^a	1.52	1.60	1.37	1.14	0.87	0.64	0.41	1.22	0.92	0.62	0.25	0.55	0.85
GaSb	0.81	1.37	1.17	0.97	0.91	0.71	0.51	1.04	0.79	0.53	-0.04	0.21	0.47
InP	1.42	1.49	1.27	1.06	0.82	0.60	0.39	1.14	0.86	0.58	0.77	1.05	1.33
InAs	0.42	1.41	1.21	1.00	0.52	0.32	0.11	1.08	0.81	0.55	0.45	0.72	0.98
InSb	0.24	1.22	1.04	0.87	0.53	0.35	0.18	0.93	0.70	0.47	0.06	0.29	0.52

^aAbsolute position of energy levels adapted to experiment as described in Sec. II.

III. FERMI-LEVEL PINNING ENERGIES RELATED TO ANTISITE DEFECT LEVELS

Antisite defects near III-V semiconductor surfaces have been discussed as those native defects that produce the observed, characteristic Fermi-level pinning energies at Schottky barriers and semiconductor interfaces.^{4,5,33-35} Therefore, we compare these energies to our results for both cation and anion antisite defects. In Table V, we give the experimentally determined FLPE, which are characteristic for the III-V semiconductors and are basically independent of the adsorbed atom. Usually, two such characteristic levels have been observed for *n*-type materials, whereas only one has been reported for the few investigated *p*-type compounds.^{4,5,36-39} For comparison, we also give the FLPE which would result from our calculations for the bulk CAS and AAS defect according to the following considerations.

For *n*-type materials acceptorlike states are needed. The CAS defect offers its neutral and single-negative charge state causing Fermi-level pinning against $\epsilon(0|-)$ and $\epsilon(-|-)$, respectively. The AAS defect offers its single- and double-positive charge state causing pinning against $\epsilon(0|+)$ and $\epsilon(+|+)$, respectively. For *p*-type materials, on the other hand, donorlike states are required. Here, the CAS defect offers its single- and

double-negative charge state, the AAS defect offers its neutral and single-positive charge state. This results in FLPE approximately equal to $\epsilon(0|-)$ and $\epsilon(-|-)$ for CAS defects and $\epsilon(0|+)$ and $\epsilon(+|+)$ for AAS defects.

Inspection of Table V shows that for some materials the proper levels of both the CAS and the AAS defect lie rather close to the FLPE. However, if one assumes that only one type of defect is mainly responsible for the observed pinning levels, the cation antisite defect has to be clearly favored. Only the CAS defect is able to reproduce the *trends* of all experimental data almost quantitatively whereas the *trends* predicted with the AAS defect are in worse agreement with the FLPE. For GaSb, this disagreement is significant, where the AAS defect would predict the pinning energies close to or in the conduction band whereas experiments give them closer to the valence band, which is in agreement with the predictions made via the CAS defect.

It should be particularly mentioned that for InAs both the *p*-type and *n*-type pinning level have been reported to be in the conduction band which is in agreement with CAS defect interpretation which gives all possible pinning levels far into the conduction band.^{36,37}

The fact that the energy levels for the bulk CAS defects agree so well with the characteristic FLPE at surfaces and interfaces may be somewhat surprising at first. However, recent total-energy calculations have shown that adsorbed atoms tend to reestablish the unreconstructed surface again.⁴⁰ We also want to note that the CAS defect model is consistent with typical properties of the observed pinning energies. The existence of two characteristic pinning levels for *n*-type compounds can be explained by the creation of the CAS defect in the originally preferentially neutral or single-negative charge state depending on the character of the adsorbed atoms. The fact that only one characteristic pinning level has been found for every investigated *p*-type compound indicates that the CAS defect is not likely to be produced in the originally double-negative charge state. Furthermore, experiments seem to show that in all cases where two different pinning levels exist for the *n*-type material the lower one is identical in energy with the one observed for the *p*-type material (see, e.g., Table V). This also confirms that one and the same defect (in different charge states) is responsible for the observed typical FLPE in both *n*- and *p*-type compounds. The switching of the *n*-type pinning level to the value of the *p*-type pinning level has been explicitly observed for Au layers of varying thickness on GaAs(100) surfaces.⁸

Although our results strongly suggest that the cation antisite defect produces the characteristic FLPE, one should remember that we tentatively assumed that *A* and *B* are the two ionization energies associated with Ga_{As} which lead to the absolute position of our results for the CAS defects. Furthermore, Tables II and III show that the characteristic trends that made the CAS defect preferable over the AAS defect are mainly determined by the *T*₂ anion vacancy levels: Table IV shows that the interatomic matrix elements *U* do not change too much from compound to compound. As a consequence, our results show clearly that the levels produced by a defect located

TABLE V. Characteristic experimental Fermi-level pinning energies E_{pi} and those obtained with the cation (CAS) and anion (AAS) antisite defects from Table IV. The experimental values E_{pi} are from Refs. 4 and 36-39.

	E_{pi} (eV)	<i>n</i> type		<i>p</i> type
AlAs		1.15		
	AAS	0.96	0.73	0.73
	CAS	0.93	0.62	0.62
GaP	E_{pi}	1.26	1.04	
	AAS	1.24	1.00	1.00
	CAS	1.17	0.85	0.85
GaAs	E_{pi}	0.75		0.55
	AAS	0.76	0.53	0.53
	CAS	0.70	0.40	0.40
GaSb	E_{pi}	0.3	0.1	0.1
	AAS	0.81	0.61	0.61
	CAS	0.34	0.09	0.09
InP	E_{pi}	1.3	0.85	0.9
	AAS	0.71	0.50	0.50
	CAS	1.19	0.91	0.91
InAs	E_{pi}	0.48		0.49
	AAS	0.42	0.22	0.22
	CAS	0.85	0.59	0.59

at the anion site is mainly responsible for the observed position of Fermi-level pinning energies at surfaces and interfaces in agreement with Refs. 6 and 32–34. Our results, however, show that the cation antisite defect, isolated or involved in a complex, is a very probable candidate.

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- ¹J. A. Van Vechten, *J. Electrochem. Soc.* **122**, 419 (1975).
- ²J. A. Van Vechten, *J. Electrochem. Soc.* **122**, 423 (1975).
- ³E. R. Weber, H. Ennen, U. Kaufmann, J. Windscheif, J. Schneider, and T. Wosinsky, *J. Appl. Phys.* **53**, 6140 (1982).
- ⁴W. E. Spicer, P. W. Chye, P. R. Skeath, C. Y. Su, and I. Lindau, *J. Vac. Sci. Technol.* **16**, 1422 (1979).
- ⁵W. Mönch, *Proceedings of the NATO ASI on Physics of Submicron Semiconductor Devices, San Miniato, 1983* (Plenum, New York, 1983), and references therein.
- ⁶M. S. Daw and D. L. Smith, *Solid State Commun.* **37**, 205 (1981).
- ⁷R. E. Allen and J. D. Dow, *Phys. Rev. B* **25**, 1423 (1982).
- ⁸R. W. Grant, J. R. Waldrop, S. P. Kowalczyk, and E. A. Kraut, *J. Vac. Sci. Technol.* **19**, 477 (1981).
- ⁹M. Jaros, *Deep Levels in Semiconductors* (Hilger, Bristol, 1982).
- ¹⁰P. J. Lin-Chung and T. L. Reinecke, *Phys. Rev. B* **27**, 1101 (1983).
- ¹¹T. L. Reinecke, in *Proceedings of the XVI International Conference on the Physics of Semiconductors, Montpellier, 1982*, edited by M. Averous (North-Holland, Amsterdam, 1983), p. 194.
- ¹²E. S. Ho and J. D. Dow, *Phys. Rev. B* **27**, 1115 (1983).
- ¹³J. P. Buisson, R. E. Allen, J. D. Dow, *J. Phys. (Paris)* **43**, 181 (1982).
- ¹⁴W. Pötz and D. K. Ferry, *Phys. Rev. B* **29**, 5687 (1984).
- ¹⁵M. Lannoo and J. Bourgoin, *Point Defects in Semiconductors I*, Vol. 22 of *Springer Series in Solid-State Sciences*, edited by M. Cardona (Springer, Berlin, 1981).
- ¹⁶P. Vogl, in *Festkörperprobleme XXI (Advances in Solid State Physics)*, edited by J. Treusch (Vieweg, Branschweig, 1981), p. 191.
- ¹⁷C. A. Coulson and M. J. Kearsley, *Proc. R. Soc. London Ser. A* **241**, 433 (1957).
- ¹⁸W. A. Harrison, *Electronic Structure and Properties of Solids* (Freeman, San Francisco, 1980).
- ¹⁹Similarly rescaled atomic orbital energies have been used in P. Vogl, H. P. Hjalmarson, and J. D. Dow, *J. Phys. Chem. Solids* **44**, 365 (1983) to fit the band structure of perfect semiconductors.
- ²⁰A. G. Milnes and D. L. Feucht, *Heterojunctions and Metal-Semiconductor Junctions* (Academic, New York, 1972).
- ²¹M. Neuberger, *Handbook of Electronic Materials II: III-V Semiconducting Compounds* (Plenum, New York, 1971).
- ²²T. A. Carlson, *Photoelectron and Auger Spectroscopy* (Plenum, New York, 1975).
- ²³Only those levels are considered which are expected to lie in or close to the main energy gap. The sometimes considerable differences in the results of the two different TB calculations used for comparison may be due to the different approaches and input parameters used.
- ²⁴B. K. Meyer, J.-M. Spaeth, and M. Scheffler, *Phys. Rev. Lett.* **52**, 851 (1984).
- ²⁵U. Kaufman, J. Schneider, and A. Räuber, *Appl. Phys. Lett.* **29**, 312 (1976).
- ²⁶R. J. Wagner, J. J. Krebs, G. H. Stauss, and A. M. White, *Solid State Commun.* **36**, 15 (1980).
- ²⁷U. Kaufmann, J. Schneider, R. Wörner, T. A. Kennedy, and N. D. Wilsey, *J. Phys. C* **14**, L951 (1981).
- ²⁸J. C. Slater, *Quantum Theory of Molecules and Solids IV* (McGraw-Hill, New York, 1974).
- ²⁹D. V. Lang, R. A. Logan, and L. C. Kimerling, *Phys. Rev. B* **15**, 4874 (1977).
- ³⁰S. Loualiche, A. Nouailhat, G. Guillot, M. Gavand, and A. Laugier, *J. Appl. Phys.* **53**, 8691 (1982).
- ³¹J. Schnider, in *Proceedings of the 2nd Conference on Semi-Insulating III-V Materials, Evian (France), 1982*, edited by S. Makram-Ebeid and B. Tuck (Shivo, Nantwich, 1982), p. 144.
- ³²J. P. Buisson, R. E. Allen, and J. D. Dow, *Solid State Commun.* **43**, 833 (1982).
- ³³R. E. Allen and J. D. Dow, *Phys. Rev. B* **25**, 1423 (1982).
- ³⁴R. E. Allen and J. D. Dow, *Solid State Commun.* **45**, 379 (1983).
- ³⁵A. D. Katnani, G. Margaritondo, R. E. Allen, and J. D. Dow, *Solid State Commun.* **44**, 1231 (1982).
- ³⁶H. H. Wieder, *Appl. Phys. Lett.* **38**, 170 (1981).
- ³⁷S. Kawaji and Y. Kawaguchi, *J. Phys. Soc. Jpn.* **21**, 336 (1966).
- ³⁸L. J. Brillson, *Phys. Rev. Lett.* **40**, 1378 (1978).
- ³⁹C. A. Mead and W. G. Spitzer, *Phys. Rev. A* **134**, 713 (1964).
- ⁴⁰J. Ihm and J. D. Joannopoulos, *J. Vac. Sci. Technol.* **21**, 340 (1982).