

Relationships between the band gaps of the zinc-blende and wurtzite modifications of semiconductors

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While the direct band gaps of wurtzite (W) and zinc-blende (ZB) structures are rather similar, the W and ZB gaps can differ enormously (e.g., ~ 1 eV in SiC) in indirect gap materials. This large difference is surprising given that the structural difference between wurtzite and zinc blende starts only in the third neighbor and that *total* energy differences are only ~ 0.01 eV/atom. We show that zinc-blende compounds can be divided into five types (I–V) in terms of the order of their Γ_{1c} , X_{1c} , and L_{1c} levels and that this decides the character (direct, indirect, pseudodirect) of the wurtzite band gap. The observation of small $E_g^W - E_g^{ZB}$ differences in direct band-gap systems (“type II,” e.g., ZnS), and large differences in indirect gap systems (“type IV,” e.g., SiC) are explained. We further show that while both type-III systems (e.g., AlN) and type-V systems (e.g., GaP) have an indirect gap in the zinc-blende form, their wurtzite form will have direct and pseudodirect band gaps, respectively. Furthermore, a direct-to-pseudodirect transition is predicted to occur in type-I (e.g., GaSb) systems.

The most common crystal structures of binary octet semiconductors—the zinc blende (ZB) and wurtzite (W)—differ structurally only in their *third*-nearest-neighbor atomic arrangement. Concomitantly with this subtle difference, the calculated¹ wurtzite–zinc-blende *total* energy difference $E_{\text{tot}}^W - E_{\text{tot}}^{ZB}$ is only ~ 0.01 eV/atom. Because of this small energy difference, a number of semiconductors can be prepared in both crystal forms by subtle variations in the growth temperature² or by altering the substrate.³ Measurements of the lowest-energy wurtzite and zinc-blende band gaps in many II–VI compounds also reveal small differences⁴ ($E_g^W - E_g^{ZB} \sim 0.1$ eV). Surprisingly, however, in SiC, $E_g^W - E_g^{ZB} \sim 1$ eV.^{5,6} This appears to be a huge value, given that the difference in the wurtzite vs zinc-blende local atomic arrangements starts only in the third neighbor and that the calculated¹ W vs ZB total energy difference for SiC is only 0.003 eV/atom. We have previously shown¹ that the trends in the total energy difference $E_{\text{tot}}^W - E_{\text{tot}}^{ZB}$ among all binary semiconductors⁷ can be accurately explained in terms of (quantum-mechanically defined) *atomic radii*.⁸ Here we explain the trends in the band-gap difference $E_g^W - E_g^{ZB}$ in terms of band folding and crystal symmetry. We show that given the relative order of the Γ_{1c} , X_{1c} , and L_{1c} conduction-band states in *zinc blende*, we can predict the ensuing band structure *type* (e.g., direct, pseudodirect, or indirect) of the *wurtzite* counterpart. We divide the binary octet semiconductors into five types (I–V) according to the relative order of the zinc-blende conduction states. Direct first-principles band-structure calculations on 17 compounds in both crystal structures establish the appropriateness of this classification. The observation of small $E_g^W - E_g^{ZB}$ differences in direct band-gap system (“type-II,” e.g., ZnS), and large differences in indirect gap systems (“type IV,” e.g., SiC) are explained. We further show that while both type-III systems (e.g., AlN) and type-V systems (e.g., GaP) have an indirect gap in the zinc-blende form, their wurtzite form will have direct⁹ and

pseudodirect band gaps, respectively. Furthermore, a direct-to-pseudodirect transition is predicted to occur in type-I (e.g., GaSb) systems.

Our band-structure calculations were performed in the local-density approximation (LDA) using the Ceperley–Alder exchange correlation, as parametrized by Perdew and Zunger.¹⁰ Measured⁴ structural parameters were used in the band-structure calculations.¹¹ We use the linearized-augmented-plane-wave (LAPW) method¹² for systems for which chemically active localized orbitals exist (all II–VI’s as well as the III–V nitride), while for all other systems we used the pseudopotential plane-wave method,¹³ generating nonlocal pseudopotential using the method of Kerker,¹⁴ including the “core correction.”¹⁵ The kinetic-energy basis-set cutoff value is 20 Ry. Table I gives the lowest conduction-band energy levels at the main high-symmetry points of the zinc-blende and wurtzite structures of 17 compounds. (A good depiction of the respective Brillouin zones is given in Fig. 2 of Ref. 16.) Our results agree with previous calculations¹⁷ except for GaN and InN for which previous pseudopotential calculations¹⁸ excluded cation *d* states, thus producing significant errors relative to our all-electron calculations. We made no attempt to correct in Table I the LDA errors.^{10,19} These are apparent when comparing trends in a homological chemical series of zinc-blende compounds. For example, while the LDA correctly predicts the (unexpected but experimentally observed⁴) *increase* in band gap of sulfides relative to oxides (a consequence of *p-d* coupling²⁰), Table I shows that the LDA fails to produce the experimentally observed⁴ monotonic *decrease* in band gaps E_g^{ZB} in the $MS \rightarrow MSe \rightarrow MTe$ ($M = \text{Zn, Cd}$) zinc-blende series. Thus, the LDA underestimation of the band gap seems to increase with ionicity. Fortunately, however, the LDA errors are mostly canceled when comparing the corresponding electronic states of the two crystal modifications of the same chemical compound. For example, the calculated difference $E_g^W - E_g^{ZB}$ in minimum-energy gaps in SiC is 0.83 eV (measured:^{5,6} 0.94

TABLE I. LDA calculated conduction-band energies (in eV, relative to valence-band maximum) at some high-symmetry points of zinc-blende and wurtzite semiconductors. Results are calculated at the experimental lattice constants (Ref. 4) a_0 (in Å) using the LAPW (L) method or the pseudopotential (P) method with core correction. In both cases, we use the LDA exchange-correlation potential of Ref. 10. An asterisk denotes the lowest band gap.

Type	Compounds	a_0 (Å)	Zinc-blende eigenvalues (eV)			Wurtzite eigenvalues (eV)			
			Γ_{1c}	X_{1c}	L_{1c}	$\bar{\Gamma}_{1c}$	$\bar{\Gamma}_{3c}$	\bar{M}_{1c}	\bar{U}_{1c}
I	GaSb(P)	6.0959	0.12*	0.82	0.39	0.13	0.02*	0.67	0.54
II	GaN(L)	4.5094	1.76*	3.29	4.56	1.91*	4.18	4.94	4.01
II	GaAs(P)	5.6532	0.44*	1.36	0.94	0.47*	0.57	1.20	1.05
II	InN(L)	4.9882	-0.38*	2.87	3.04	-0.26*	2.78	3.76	3.04
II	ZnO(L)	4.5707	0.63*	5.18	5.35	0.71*	5.14	5.67	5.31
II	ZnS(L)	5.4102	1.86*	3.22	3.09	1.95*	2.86	3.47	3.16
II	ZnSe(L)	5.6676	1.05*	2.84	2.36	1.10*	2.12	2.93	2.56
II	ZnTe(L)	6.0990	1.04*	2.17	1.64	1.04*	1.35	1.98	1.82
II	CdO(L)	5.4217	-0.41*	4.62	3.51	-0.36*	3.39	3.63	3.81
II	CdS(L)	5.8180	0.87*	3.32	2.76	0.94*	2.58	3.51	3.01
II	CdSe(L)	6.0840	0.31*	2.96	2.16	0.38*	1.99	3.02	2.51
II	CdTe(L)	6.4810	0.50*	2.49	1.63	0.54*	1.43	2.30	1.94
III	AlN(L)	4.3714	4.24	3.25*	7.28	4.36*	6.88	5.66	4.90
IV	AlAs(P)	5.6600	1.90	1.35*	2.02	1.93	1.64	1.62*	1.66
IV	AIP(P)	5.4670	3.10	1.50*	2.69	3.14	2.27	1.83*	2.03
IV	SiC ^a (L)	4.3590	6.30	1.32*	5.39	6.31	4.67	2.64	2.98
V	GaP(P)	5.4506	1.76	1.56*	1.63	1.81	1.23*	1.42	1.51

^aSiC in the wurtzite structure has a minimum LDA energy gap of 2.15 eV at \bar{K} .

eV) while for ZnS and ZnSe we find differences of 0.09 and 0.05 eV compared with the measured values 0.08 (Ref. 21) and 0.05 eV,²² respectively.

We next develop a number of rules [(a)–(c) below] that explain the generic relation between zinc-blende and wurtzite electronic states. When viewed from the zinc-blende [111] crystal axis (or the wurtzite [0001] crystal axis), the zinc-blende and wurtzite lattices can be considered as *layered superstructures*⁵ (see figures in Ref. 1). Thus, along the [111]

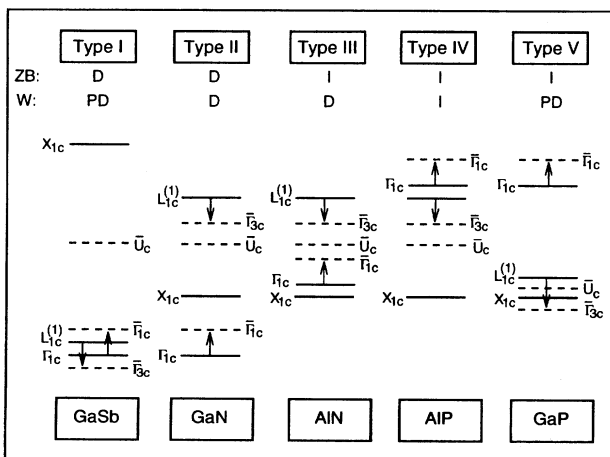


FIG. 1. LDA calculated wurtzite gap at $\bar{\Gamma}_{1c}$ vs the zinc-blende gap at Γ_{1c} .

axis there are *exact* folding relationships between the two structures.¹⁶ Since the hexagonal wurtzite structure has 4 atoms/cell while the cubic zinc-blende structure has 2 atoms/cell, there are twice as many bands per k points in the wurtzite structure. Consequently, two k points on the zinc-blende Γ - L^\perp line fold onto one k point in the $\bar{\Gamma}$ - \bar{A} line of the hexagonal Brillouin zone. In particular, we have

$$\Gamma_1 \rightarrow \bar{\Gamma}_1(\Gamma_1), \quad \Gamma_{15} \rightarrow \bar{\Gamma}_1(\Gamma_{15}) + \bar{\Gamma}_6(\Gamma_{15}), \quad (1)$$

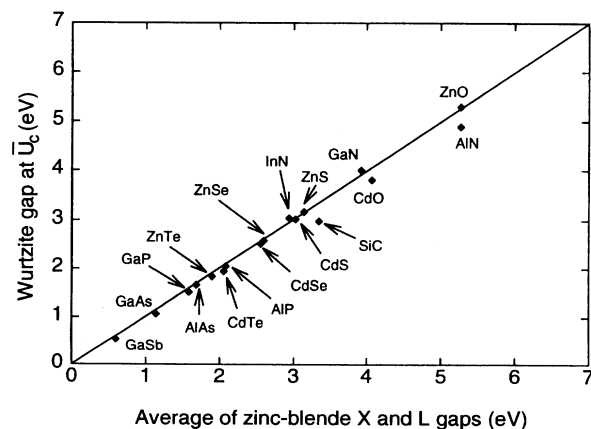


FIG. 2. LDA calculated wurtzite gap at \bar{U}_c vs the average of zinc-blende X and L gaps.

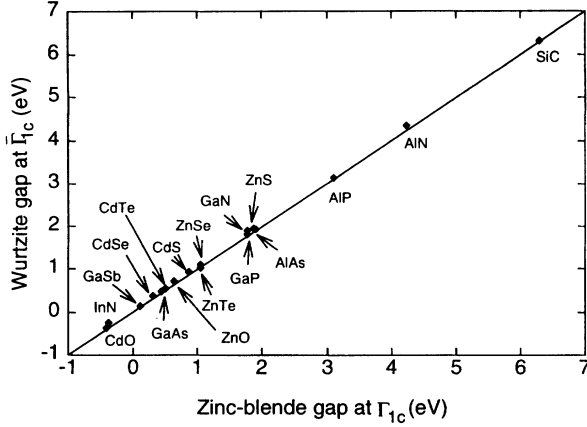


FIG. 3. Illustration of how the zinc-blende energy levels (solid lines) are modified by rules (a)–(c) (vertical arrows) to yield the wurtzite energy levels (dashed lines). Types I and II are direct (*D*) in zinc-blende structure while types III, IV, and V are indirect (*I*) in zinc-blende structure. Types I and V are pseudodirect (*PD*) in the wurtzite structure.

$$L_1 \rightarrow \bar{\Gamma}_3(L_1), \quad L_3 \rightarrow \bar{\Gamma}_5(L_3).$$

Here, we denote wurtzite states by an overbar and indicate in parentheses the parent zinc-blende states. After folding, states of the *same* symmetry can interact and thus repel each other with magnitude that in perturbation theory is inversely proportional to their initial energy difference and directly proportional to the square of their coupling matrix element V .² This leads to two simple rules.

(a) *The wurtzite and zinc-blende Γ_{1c} gaps are very similar, with the wurtzite gap being slightly but systematically larger.* This rule stems from the fact that the $\bar{\Gamma}_{1v}(\Gamma_{15v})$ – $\bar{\Gamma}_{1c}(\Gamma_{1c})$ energy levels repel only weakly because the parent zinc-blende states Γ_{15v} and Γ_{1c} have different orbital characters (*p*-*d* and *s*, respectively), thus small V .² Furthermore, the upward repulsion of $\bar{\Gamma}_{1c}$ is partially canceled by a crystal-field splitting in the valence band. The net effect is that the direct wurtzite band gap is equal to or slightly larger than the direct zinc-blende band gap. This is illustrated by direct LDA calculations in Fig. 1.

(b) $\bar{\Gamma}_{3c}(L_{1c}^{(1)})$ is below the parent zinc-blende $L_{1c}^{(1)}$ state. This rule reflects the fact that the coupling between the lowest L_{1c}^{\perp} folded states $\bar{\Gamma}_{3c}(L_{1c}^{(1)})$ and the higher L_{1c}^{\perp} folded $\bar{\Gamma}_{3c}(L_{1c})$ states is strong since the various L_{1c} states have similar *s* and *p* orbital characters. Thus, $\bar{\Gamma}_{3c}(L_{1c}^{(1)})$ is pushed below the zinc-blende parent $L_{1c}^{(1)}$. This is illustrated in Table I.

Away from the [111] line in the zinc-blende Brillouin zone there are no exact folding relationships. However, in some cases one can still use the approximate folding relations¹⁶ to derive the relationships between zinc-blende and wurtzite energy levels. For example, the zinc-blende L^{\parallel} and X points project onto the point \bar{U} (two-thirds of the \bar{M} – \bar{L} distance away from \bar{M}). This leads to “the energy averaging rule.”

(c) *The wurtzite energy at \bar{U}_c is the average of the zinc-blende L_{1c} and X_{1c} energies:*

$$E(\bar{U}_c) \cong \frac{1}{2}[E(L_{1c}) + E(X_{1c})]. \quad (2)$$

This rule is demonstrated by LDA calculations in Fig. 2. In the following analysis we will use the wurtzite \bar{U}_c gap $E(\bar{U}_c)$ as a characteristic indirect gap in the wurtzite structure. As Table I shows, in some indirect gap wurtzite systems the conduction-band minimum often occurs at the \bar{M} point (\bar{K} point for SiC). However, conduction-band minima at \bar{M} and \bar{K} are closer to the \bar{U} energy than to the $\bar{\Gamma}$ energy.

Using rules (a)–(c) we can now predict the relative order of wurtzite states in terms of the relative order of their zinc-blende Γ_{1c} , X_{1c} , and L_{1c} levels.²³ This is illustrated in Fig. 1. Using rule (a) we position $\bar{\Gamma}_{1c}(\Gamma_{1c})$ slightly above Γ_{1c} . Next, using rule (b) we position $\bar{\Gamma}_{3c}(L_{1c}^{(1)})$ below $L_{1c}^{(1)}$. Finally, using rule (c) we place \bar{U}_c exactly in the middle of $L_{1c}^{(1)}$ and X_{1c} . This analysis orders the binary octet semiconductors studied here into five types (I–V).

(i) Type-I compounds (e.g., GaSb): Here, the zinc-blende compound is direct at Γ_{1c} , but the L_{1c} state is so close to the Γ_{1c} conduction-band minimum²⁴ that the upwards shift of $\bar{\Gamma}_{1c}$ and the downwards shift of $\bar{\Gamma}_{3c}$ in the wurtzite structure [rules (a) and (b)] reverse the order of these levels, making the wurtzite compound pseudodirect at $\bar{\Gamma}_{3c}$. We find that this happens in GaSb.²³

(ii) Type-II compounds (e.g., GaN, GaAs, InN, Zn, and Cd chalcogenides): These compounds also have direct Γ_{1c} conduction-band minimum (CBM) in the zinc-blende structure but now the L_{1c} state is well above Γ_{1c} .²⁴ In this case rule (a) predicts that the corresponding wurtzite compound will also be direct, with a slightly larger gap. The compounds ZnS (Ref. 21) and ZnSe (Ref. 22) with observed^{4,21,22} small positive $E_g^W - E_g^{ZB}$ values belong to this type.

(iii) Type-III compounds (e.g., AlN): Here, the zinc-blende compound has a CBM at X_{1c} which is close to Γ_{1c} , but L_{1c} is at a much higher energy than both. In this case, rule (c) places the wurtzite conduction-band state \bar{U}_c above $\bar{\Gamma}_{1c}$. Hence, the wurtzite compound will be direct despite the fact that the zinc blende is indirect. This indirect-to-direct conversion is found to occur in AlN, in which the conduction-band minimum is $\bar{\Gamma}_{1c}(\Gamma_{1c})$. This was noted previously by Rubio *et al.*⁹ in their quasiparticle calculation.

(iv) Type-IV compounds (e.g., AlP, AlAs, SiC): These zinc-blende compounds have CBM at X_{1c} with the Γ_{1c} and L_{1c} at much higher energy than X_{1c} , and Γ_{1c} is closer to L_{1c} than to X_{1c} . In this case, rules (a)–(c) predict that the wurtzite compound will also be indirect with a higher gap than zinc blende. We find that most of the compounds in this group have a conduction-band minimum at \bar{M} , except SiC which has a minimum at \bar{K} (about 0.5 eV below the energy minimum at \bar{M}). This explains the observed $E_g^W \gg E_g^{ZB}$ in SiC.

(v) Type-V compounds (e.g., GaP): Here either the zinc-blende compounds have a CBM at X_{1c} with the energy of L_{1c} being close by, or the CBM is at L_{1c} .²⁵ In this case, level repulsion in the wurtzite structure [rule (b)] makes the L -folded $\bar{\Gamma}_3(L_{1c}^{(1)})$ the conduction-band minimum, hence, the compounds become pseudodirect. This indirect-pseudodirect

transition is predicted for GaP where $L_{1c}^{(1)}$ state is close to the conduction-band minimum at X_{1c} (see Table I).

In summary, we have found three simple rules to predict the basic band-structure type of a wurtzite octet compound from its zinc-blende energy levels. We explained the small direct band-gap differences between the zinc-blende and wurtzite structure in a type-II system and large indirect gap differences in a type-IV system. We also predict that as the lattice changes from zinc blende to wurtzite an indirect-to-

direct transition will occur in AlN, an indirect-to-pseudodirect transition will occur in GaP, and a direct-to-pseudodirect transition will occur in GaSb. Experimental investigations on these predictions are called for.

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- ¹C.-Y. Yeh, Z. W. Lu, S. Froyen, and A. Zunger, *Phys. Rev. B* **45**, 12 130 (1992); **46**, 10 086 (1992).
- ²V. A. Fedorov, V. A. Ganshin, and Yu. N. Korkishko, *Phys. Status Solidi A* **126**, K5 (1991); Y. M. Romyantsev, F. A. Kuznetsov, and S. A. Stroitelev, *Kristallografiya* **10**, 263 (1965) [*Sov. Phys. Crystallogr.* **10**, 212 (1965)].
- ³W. M. Yim and E. J. Stofko, *J. Electrochem. Soc. Solid-State Sci. Technol.* **119**, 381 (1972).
- ⁴*Numerical Data and Functional Relationships in Science and Technology*, edited by O. Madelung, M. Schulz, and H. Weiss, Landolt-Bornstein, New Series, Group III, Vol. 17, Pts. a and b (Springer-Verlag, Berlin, 1982).
- ⁵L. Patrick, D. R. Hamilton, and W. J. Choyke, *Phys. Rev.* **143**, 526 (1966).
- ⁶R. G. Humphreys, D. Bimberg, and W. J. Choyke, *J. Phys. Soc. Jpn. Suppl. A* **49**, 519 (1980).
- ⁷Both our highly converged pseudopotential and LAPW calculations yield for GaN $E_{\text{tot}}^{\text{W}} - E_{\text{tot}}^{\text{ZB}} = -10$ meV/atom, predicting that the ground state of GaN is wurtzite. B. J. Min *et al.* [*Phys. Rev. B* **45**, 1159 (1992)], however, found in their pseudopotential calculation that the ground state of GaN is zinc blende ($E_{\text{tot}}^{\text{W}} - E_{\text{tot}}^{\text{ZB}} = +9.5$ meV/atom), in contradiction with our results. Their calculated equilibrium lattice constant (3.043 Å) is also much smaller compared with the experimental value (3.192 Å). We believe that their results are less accurate due to the lack of core correction in their pseudopotential calculation.
- ⁸A. Zunger, *Phys. Rev. B* **22**, 5839 (1980).
- ⁹A. Rubio, J. L. Corkill, M. L. Cohen, E. L. Shirley, and S. G. Louie, *Phys. Rev. B* **48**, 11 810 (1993).
- ¹⁰D. M. Ceperly and B. J. Alder, *Phys. Rev. Lett.* **45**, 566 (1980); J. P. Perdew and A. Zunger, *Phys. Rev. B* **23**, 5048 (1981).
- ¹¹We use the experimental bond lengths $R = (\sqrt{3}/4)a_0$ for both structures, where a_0 is the cubic lattice constant given in Table I. We further use the ideal wurtzite parameters $c/a = 1.633$ and $u = 0.375$.
- ¹²S.-H. Wei and H. Krakauer, *Phys. Rev. Lett.* **55**, 1200 (1985), and references therein.
- ¹³J. Ihm, A. Zunger, and M. L. Cohen, *J. Phys. C* **12**, 4409 (1979).
- ¹⁴G. P. Kerker, *J. Phys. C* **13**, L189 (1980).
- ¹⁵S. Louie, S. Froyen, and M. Cohen, *Phys. Rev. B* **26**, 1738 (1982).
- ¹⁶M. R. Salehpour and S. Satpathy, *Phys. Rev. B* **41**, 3048 (1990).
- ¹⁷N. E. Christensen and O. B. Christensen, *Phys. Rev. B* **33**, 4739 (1986); S. B. Zhang, D. Tomanek, M. L. Cohen, and S. G. Louie, *ibid.* **40**, 3162 (1989); V. Fiorentini, M. Methfessel, and M. Scheffler, *ibid.* **47**, 13 353 (1993).
- ¹⁸B. J. Min, C. T. Chan, and K. M. Ho, *Phys. Rev. B* **45**, 1159 (1992); P. E. Van Camp, V. E. Van Doren, and J. T. Devreese, *ibid.* **44**, 9056 (1991); K. Miwa and A. Fukumoto, *ibid.* **48**, 7897 (1993).
- ¹⁹A. Zunger and A. J. Freeman, *Phys. Rev. B* **16**, 290 (1977).
- ²⁰S.-H. Wei and A. Zunger, *Phys. Rev. B* **37**, 8958 (1988), and references therein.
- ²¹D. Theis, *Phys. Status Solidi* **79B**, 125 (1977); R. G. Wheeler and J. C. Miklosz, *7th International Conference on the Physics of Semiconductors* (Dunod, Paris, 1964), p. 873.
- ²²G. Hitier, Thesis, Paris VI, 1980.
- ²³LDA errors are not uniform at different k points in the Brillouin zone. These errors are larger at Γ_{1c} (relative to the valence-band maximum), but smaller at X_{1c} and L_{1c} . This k dependence of the error may change the order of energy levels of a real material from our LDA prediction. Our estimation of the LDA error suggests that GaAs in wurtzite structure may have a pseudodirect gap (type I), instead of direct gap (type II) predicted by the LDA. For other compounds in Table I, we believe the LDA correction will not change the *type* of the band gaps. In any case, rules (a)–(c) are intrinsic.
- ²⁴In type-I and type-II systems, the X_{1c} state can be anywhere above Γ_{1c} .
- ²⁵In the type-V system, the Γ_{1c} state can be anywhere above the conduction-band minimum.