PHYSICAL REVIEW B **73**, 245206 (2006)

Ab initio all-electron calculation of absolute volume deformation potentials of IV-IV, III-V, and II-VI semiconductors: The chemical trends

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(Received 24 March 2006; published 13 June 2006)

We calculate systematically the absolute volume deformation potential (AVDP) of the Γ_{8v} valence band maximum (VBM) and the Γ_{6c} conduction band minimum (CBM) states for all group IV, III-V, and II-VI semiconductors. Unlike previous calculations that involve various assumptions, the AVDPs are calculated using a recently developed approach that is independent of the selection of the reference energy levels. We find that although the volume deformation potentials of the CBM state are usually large and always negative, those of the VBM state are usually small and always positive. The AVDP of the VBM state decreases as the *p-d* coupling increases, e.g., in the II-VI compounds. The AVDP of CBM decreases as the ionicity increases. Our calculated chemical trends of the AVDPs are explained in terms of the atomic orbital energy levels and coupling between these orbitals.

DOI: 10.1103/PhysRevB.73.245206 PACS number(s): 71.20.Nr, 71.15.Dx

I. INTRODUCTION

The absolute volume deformation potential (AVDP) $a_v^i = dE^i/d\ln v$ for state i describes the shift of individual energy level E_i with respect to an absolute energy reference (e.g., vacuum) in a crystal under a volume deformation.[1,2] a_v^i is an important physical parameter for semiconductors because in order to assess quantum confinement for holes, and separately for electrons in strained heterostructure quantum dots and quantum wells, it is necessary to know the natural band offsets[3] and the AVDPs for the valence band maximum (VBM), and separately for the conduction band minimum (CBM) states.[4–6] The AVDP is also an important fitting parameter in generating empirical pseudopotentials that has good transferability in calculating the band structure of lattice-mismatched semiconductor alloys and superlattices.[7] Furthermore, study of the AVDP also provides important information on the individual wave function characters of the energy levels.[8] However, despite the importance, the exact value of the AVDP is difficult to obtain either experimentally[9–11] or theoretically.[12,14,15] Experimentally, the measured values are strongly influenced by the presence of surfaces or interfaces[11] and in most cases empirical rules (e.g., the deep-defect level pinning rule[9,10]) are assumed. Theoretically, although it is easy to calculate the difference of the AVDPs between two energy levels[15] (e.g., between the CBM and the VBM states, i.e., the band gap) using first-principles band structure method, it is difficult to obtain the AVDP of a single state. This is because modern band structure method usually applies the periodic boundary condition, so that the absolute position of an energy level in an infinity periodic crystal is only defined within an unknown constant.[16] To overcome this problem, various approximations have been assumed.[12–15,17–20] For example, Van de Walle[14] calculated the AVDP using the model-solid pseudopotential, which assumes that the crystal potential is a direct superposition of the neutral atomic pseudopotentials. Cardona and Christensen[12] assumed that the dielectric midgap energy level can be used as a constant reference. Wei and Zunger[15] have calculated the AVDPs by assuming that the energy level of the deep core state is not sensitive to the volume deformation. However, these assumptions have not been rigorously proved to be valid. The obtained values based on these assumptions often contradict each other. For example, the calculated AVDPs are all positive in Ref. 14, but are all negative in Ref. 12, whereas the values obtained in Ref. 15 are both positive and negative.

Recently, we proposed a new approach to calculate the hydrostatic AVDP using an *ab initio* all-electron method without *a priori* assumption.[21] We show that using this approach the calculated AVDP is a well-defined bulk property, i.e., independent of the reference energy levels. In this paper, we apply this new approach to calculate the AVDP of the Γ_{8v} VBM and Γ_{6c} CBM states for all group IV, III-V, and II-VI semiconductors. The general chemical trends of the calculated AVDPs are investigated. We find that (1) the core level AVDP is not negligible; (2) the volume deformation potentials for the VBM state, a_v^{VBM}, are small but all positive, whereas (3) a_v^{CBM} are usually large and all negative. (4) a_v^{VBM} decreases when the coupling between the occupied cation d orbital and the anion p orbital increases, whereas (5) a_v^{CBM} decreases when the ionicity of the compound increases. In Sec. II, we discuss briefly our calculation method. In Sec. III, we present our calculated results and discuss the general chemical trends of the AVDP for the VBM and CBM states. Finally, we summarize our results in Sec. IV.

II. METHODS OF CALCULATION

The calculation is performed at the experimental lattice constants[15,22] using the local density approximation (LDA)[23] as implemented in the WIEN2K linearized augmented plane wave code.[24] High cutoff energy for the basis functions and large number of k-points sampling for the Brillouin zone integration are used to ensure the convergence of the calculated results with respect to these parameters. To improve the flexibility of the basis functions, local orbitals[25] are used for Ge, Sn, Ga, In, Zn, Cd, and Hg valence or semicore *d* states. To obtain the AVDP of the VBM state, we use the recently developed approach described in detail in Ref. 21. Here, we give a brief description of the procedures. First, we calculate the volume deformation potential of the energy difference between the VBM and a core level $d(E_{\mathrm{VBM}}-E_{\mathrm{core}})/d\ln v$ (similarly for CBM) by expanding and compressing the cubic lattice constant separately by about 1%. Second, we calculate the uniaxial core level absolute deformation potential by constructing (n,n) homojunction superlattices[13,17,19] along three directions [100], [110], and [111]. One side of these superlattices is compressed along the superlattice direction by 1%, and the other side is expanded by 1%. The atoms at the interfaces between the expanded and compressed region are fixed at their ideal zinc-blende (ZB) position, whereas the internal structural parameters are relaxed by the valance force field (VFF) method.[26] For the polar orientations such as [100] and [111], both anion- and cation-terminated superlattices are constructed, and the results are averaged to remove the built-in electric field. The period of the superlattice n is increased until all the calculated AVDPs are converged to within 0.1 eV. We find that for the [110] superlattice, $n=10$ is required, whereas for [100] and [111] directions, we could use $n=6$. Finally, to obtain the hydrostatic AVDP for the core level, as well as the VBM and the CBM states, we average the uniaxial deformation potentials over all the directions. This average is facilitated by using the cubic symmetry of the crystal, expanding the physical property in terms of lattice harmonics.[21,27] For $l_{\max}=4$, we have

$$\bar{p}=(4p_{110}+p_{100})/5, \tag{1}$$

and for $l_{\max}=6$, we have

$$\bar{p}=(10p_{100}+16p_{110}+9p_{111})/35. \tag{2}$$

The convergence of the lattice harmonic expansion can be checked by comparing the results obtained from Eq. (1) and Eq. (2). We find that for all the calculated values, the results obtained from Eq. (1) are converged to within 0.2 eV. We want to point out that this procedure can only be used to calculate the AVDP of the core state, because they are localized on the atomic site. We cannot use this procedure to directly calculate the AVDP of the VBM or CBM state, because in a finite size superlattice calculation, the VBM or CBM wave function is not localized in one side of the superlattice, i.e., we cannot identify the VBM and CBM eigenstate energies on each side of the superlattice.

It is well known that the LDA calculation underestimates the band gap, which in turn also affects the calculated deformation potentials.[15,28] To correct the LDA error for the CBM state, we have adopted a simple method proposed by Christensen[28] by adding an external potential[15] to the LDA potential in solving the self-consistent LDA Schrödinger equations, so that the corrected band gaps are similar to experimental data.[22] For InN and HgSe, whose band gap is currently under debate, we have used this method to predict their band gaps.[15,29,30] This resulted in a band gap of about 0.7 eV for ZB InN and −0.24 eV for ZB HgSe; both are in good agreement with recent experimental data.[31–33]

III. RESULTS AND CHEMICAL TRENDS OF AVDP

Table I lists the calculated AVDPs of VBM (Γ_{8v}) and CBM (Γ_{6c}) states for all group IV, III-V, and II-V semiconductors, and the uniaxial absolute deformation potential of VBM along [100], [110], and [111] directions. For the uniaxial absolute deformation potential, the splitting at the VBM is not included. The AVDPs are calculated using Eq. (1). From the values given in Table I, the volume deformation potential of the band gap can be obtained by taking the difference between a_v^{CBM} and a_v^{VBM}. The pressure coefficients, $a_p=dE/dp$ of the energy levels and band gaps can be obtained by using the relationship $a_p=-a_v/B$, where B is the bulk modulus at the equilibrium lattice constant a_{exp}; both are given in Table I.[15,22] The values of a_v^{VBM} and a_v^{CBM} are also plotted in Fig. 1. In the following, we will analyze individually the chemical trends of AVDPs of the VBM and CBM states.

A. Absolute volume deformation potential of the Γ_{8v} state

The change of a_v^{VBM} is due to the following three effects:[15,21] (a) The kinetic energy effect. Because the kinetic energy is proportional to k^2 or $1/l^2$, where k is the reciprocal lattice vector and l is the anion-cation bond length, it increases as the volume decreases, therefore, the contribution of the kinetic energy to AVDP is negative. (b) The anion-cation *p*-*p* coupling effect. Because the VBM is a *p*-*p* bonding state,[34] the energy level decreases as the volume or bond length decreases, so its contribution to the a_v^{VBM} is always positive. The coupling is inversely proportional to the bond length and the cation-anion *p* orbital energy differences. (c) The *p*-*d* coupling effect. Due to symmetry, the anion *p* and cation *d* states in the zinc-blende structure can couple strongly with each other. If the cation *d* orbital is below the VBM, the *p*-*d* coupling contribution to a_v^{VBM} is negative, whereas it has a positive contribution if the level is unoccupied in the conduction band. Similar to the *p*-*p* coupling, the *p*-*d* coupling increases with decreasing bond length l and decreasing energy difference between the cation *d* and anion *p* orbital energies. Effects (a), (b), and (c) tend to cancel each other, so a_v^{VBM} values are usually small and the chemical trends are complex. However, we can still identify the following trends:

(1) We find that a_v^{VBM} are all positive, indicating that the *p*-*p* coupling effect is dominant. Previous calculation by some of us assumed that the core level AVDPs are zero.[15] From that assumption, they find that some of the compounds could have negative a_v^{VBM}. Our present calculations show that the AVDPs for the core states are not negligible, e.g., it is around 3 eV for GaAs. After including this core correction, we find that all a_v^{VBM} become positive and are independent to the choice of the core levels.

(2) For group VI elements, a_v^{VBM} usually decreases as the atomic number increases. This can be attributed to increased bond lengths, which reduce the *p*-*p* coupling, and the in-

TABLE I. Calculated uniaxial absolute deformation potentials (in eV) of VBM along [100], [110], and [111] directions, and the AVDPs a_v^{VBM} for VBM (Γ_{8v}) and a_v^{CBM} for CBM (Γ_{6c}) states for all group IV, III-V, and II-VI, semiconductors. The experimental lattice constants (a_{exp}, in Å) and the bulk modulus (B_{exp}, in kbar) are also given.

Compounds	a_{exp}	B_{exp}	a_{100}^{VBM}	a_{110}^{VBM}	a_{111}^{VBM}	a_v^{VBM}	a_v^{CBM}
C	3.5668	4420	1.52	2.32	2.58	2.16	−22.61
Si	5.4307	979	1.50	2.60	2.83	2.38	−10.06
Ge	5.6579	689	1.16	2.50	2.80	2.23	−7.83
Sn	6.4890	456	0.66	1.81	2.37	1.58	−6.00
BN	3.6150	3723	1.54	2.87	3.31	2.61	−15.12
AlN	4.3600	2158	2.66	4.59	5.21	4.20	−5.96
AlP	5.4635	860	1.62	2.84	3.24	2.60	−6.92
AlAs	5.6600	781	1.72	3.23	3.60	2.93	−6.00
AlSb	6.1355	551	1.44	2.97	3.63	2.65	−6.19
GaN	4.5000	2054	1.38	3.13	3.64	2.78	−4.59
GaP	5.4505	882	1.00	2.22	2.62	1.98	−6.85
GaAs	5.6533	756	1.20	2.50	3.06	2.24	−5.91
GaSb	6.0959	563	0.87	2.17	2.54	1.91	−6.10
InN	4.9800	1480	0.46	1.73	2.05	1.48	−2.18
InP	5.8687	710	0.79	2.09	2.54	1.83	−4.10
InAs	6.0583	579	0.67	2.07	2.47	1.79	−3.87
InSb	6.4794	483	0.63	1.85	2.39	1.61	−4.74
ZnO	4.6000	1520	−0.61	0.56	1.56	0.48	−1.22
ZnS	5.4102	771	−0.10	1.06	1.39	0.83	−4.33
ZnSe	5.6676	624	0.19	1.49	1.74	1.23	−3.76
ZnTe	6.0890	509	−0.07	1.25	1.53	0.99	−4.61
CdS	5.8180	620	−0.43	0.61	1.01	0.40	−2.54
CdSe	6.0520	530	0.02	1.12	1.43	0.90	−2.00
CdTe	6.4820	445	0.08	1.09	1.67	0.89	−2.81
HgS	5.8500	685	−0.62	0.44	0.79	0.23	−1.93
HgSe	6.0850	500	−0.47	0.57	0.67	0.36	−1.79
HgTe	6.4603	423	−0.43	0.66	0.97	0.44	−2.75

creased negative contribution of *p*-*d* coupling for Ge and Sn. It is interesting to note that a_v^{VBM} for C is slightly smaller than Si, even though C-C has a much smaller bond length than the Si-Si bond. This abnormal behavior could be contributed to the much more localized C 2*p* wave function compared to that of Si 3*p* wave functions, so the coupling matrix element b_{pp} for C is much smaller than for Si.

(3) For a common-anion system, the value of a_v^{VBM} decreases as the cation atomic number increases, mainly because of the reduced *p*-*p* coupling (due to increased bond length) and increased negative *p*-*d* coupling contribution.

(4) For a common cation system, when the anion atomic number increases, the cation-anion *p* orbital energy difference decreases,[15] thus it tends to increase the *p*-*p* coupling. On the other hand, the cation-anion bond length also increases, so it tends to decrease the *p*-*p* coupling. The *p*-*d* coupling also decreases when the anion atomic number increases, except for Al compounds, where it increases. Because of these factors, no clear trends are present.

(5) For II-VI Zn*X*, Cd*X*, and Hg*X* (X=S, Se, and Te), a_v^{VBM} is significantly smaller than other compounds because the negative *p*-*d* repulsion for these II-VI compounds is large. Figure 2 plots the charge density distribution of the VBM states for Si, GaAs, and ZnSe. We see that for ZnSe, the VBM state has strong *p*-*d* antibonding character. Similarly, a_v^{VBM} for Ga*X* and In*X* are smaller than for Al*Y* (Y =N, P, As, and Sb) because Al has unoccupied *d* orbitals, so for AlY, the *p*-*d* coupling contribution is positive.

B. Absolute volume deformation potential of the Γ_{6c} state

The Γ_{6c} state is the antibonding state of cation *s* and anion *s* orbitals. It moves upward in energy when the volume decreases because of (a) the increase in the kinetic energy and (b) the *s*-*s* level repulsion. The *s*-*s* coupling is inversely proportional to the bond length and the cation-anion *s* orbital energy differences. The two effects add up for this antibonding state, so a_v^{CBM} is always negative and mostly large. Because the a_v^{VBM} is usually small, the chemical trends of the band gap volume deformation potentials (a_v^{CBM}-a_v^{VBM}) are similar to that of a_v^{CBM}. We have observed the following trends for a_v^{CBM}.

(1) In the homopolar limit, where $\epsilon_s^c=\epsilon_s^a$, the magnitude of a_v^{CBM} increases rapidly when the atomic number, and thus

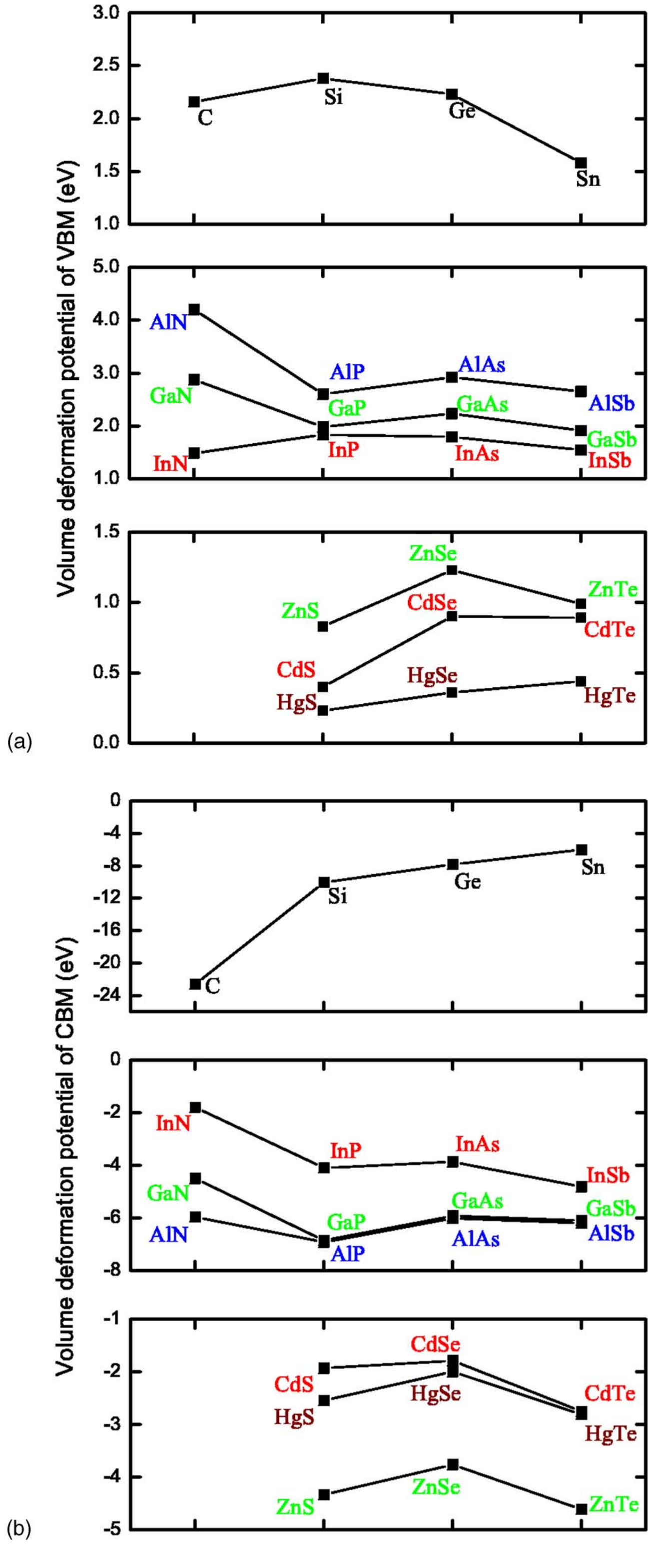

FIG. 1. (Color online) Calculated AVDPs of the VBM (a_v^{VBM}) and the CBM (a_v^{CBM}) states for group IV, III-V, and II-V semiconductors. For clarity, different scales are used for these systems.

the atomic size of the elements, decreases. For example, $-a_v^{\mathrm{CBM}}(\mathrm{C})=22.61$ eV is much larger than $-a_v^{\mathrm{CBM}}(\mathrm{Sn})=6.00$ eV. This is because the *s*-*s* level repulsion is inversely proportional to $1/l^2$.[15]

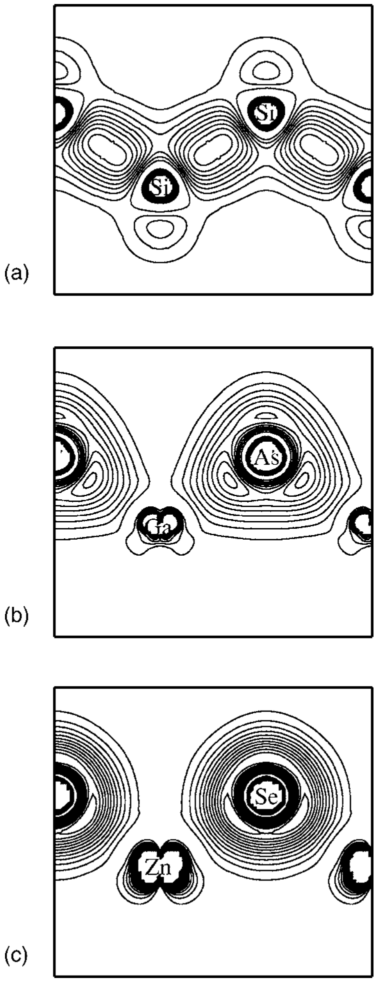

FIG. 2. Calculated charge density of VBM state for (a) Si, (b) GaAs, and (c) ZnSe. It shows that for ZnSe, the VBM has strong antibonding *p*-*d* character.

(2) For the common anion system, because the difference of the valence *s* orbital energy of the cations is relatively small,[15] the magnitude of a_v^{CBM} is mostly decided by the bond length of compounds. And because the bond length increases as the cation atomic number increases, the magnitude of a_v^{CBM} decreases as the cation atomic number increases.

(3) For the common-cation system, because the cation *s* and anion *s* orbital energy difference usually decreases as anion atomic number increases, the *s*-*s* coupling tends to increase with anion atomic number. However, this effect is partially cancelled by the increase in the bond length when the anion atomic number increases. So the variation of a_v^{CBM} with respect to the anion atomic number is not large. For example, $a_v^{\mathrm{CBM}}=-5.96$, -6.92, -6.00, and -6.19 eV for AlN, AlP, AlAs, and AlSb, respectively. The decrease of magnitude of a_v^{CBM} (AlAs) compared to a_v^{CBM} (AlP) is partly due to the fact that the As 4*s* atomic orbital energy level is lower than the P 3*s* orbital energy.[15]

(4) The magnitude of a_v^{CBM} decreases when the ionicity of the compound increases, because the $s-s$ level repulsion is inversely proportional to the energy difference between the cation *s* and anion *s* orbital energies, which increases when

the ionicity increases. For example, in III-V compounds, $-a_v^{\mathrm{CBM}}$ for nitrides is much smaller than for other III-V compounds, which is due to the large electronegativity of N (i.e., much lower N 2*s* orbital energy). This is especially true for InN, which also has relatively large bond lengths compared to AlN and GaN. Similarly, for II-VI compounds with large ionicity, e.g., ZnO, a_v^{CBM} is very small (Table I).

For most common-cation semiconductors, the direct band gap at Γ increases as the anion atomic number decreases. For example, the direct band gaps of the ZB compounds GaSb, GaAs, GaP, and GaN increase from 0.81 to 1.52 to 2.86 to 3.30 eV. However, the order is reversed between InN (E_g=0.7 eV) (Ref. 29) and InP (E_g =1.4 eV), and between ZnO (E_g=3.2 eV) and ZnS (E_g =3.8 eV) (Ref. 22) in the ZB structure. To understand this anomaly, it has been shown[29] that the increase of the band gap as the anion atomic number decreases is due to the volume deformation potential. As the anion atomic number decreases, the size of the anion also decreases. Because $a_v^{\mathrm{CBM}} - a_v^{\mathrm{VBM}}$ is always negative, the band gap increases. However, if the magnitude of a_v^{CBM} is too small, such as for the ionic InN and ZnO compounds, the volume deformation potential will not be sufficient to overcome the potential effect, which gives the opposite trend in the band gap.[29] This explains why InN has a smaller band gap than that of InP, and MO in the ZB structure has a smaller band gap than that of *M*S (*M*=Zn, Cd, and Hg).[30]

IV. SUMMARY

In summary, we have calculated the VBM and CBM absolute volume deformation potentials for all group IV, III-V, and II-VI semiconductors in ZB structure using a recently developed approach. General chemical trends of the AVDPs are revealed and explained in terms of the energy levels of the atomic orbitals and coupling between these orbitals. We find that the volume deformation potentials a_v^{VBM} are small but always positive, whereas a_v^{CBM} are all negative and mostly large. a_v^{VBM} decreases when the coupling between the occupied cation *d* orbital and the anion *p* orbital increases, whereas a_v^{CBM} decreases when the ionicity of the compound increases. Our results also explain the band gap anomaly observed in some of the ionic compounds.

ACKNOWLEDGMENTS

The work at Fudan University is supported by the National Natural Science Foundation of China, Chinese Academy of Science, and National Science Foundation of China. The work at NREL is funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, under Contract No. DE-AC36-99GO10337 to NREL.

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