Calculated spin-orbit splitting of all diamond-like and zinc-blende semiconductors: Effects of $p_{1/2}$ local orbitals and chemical trends

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We have calculated the spin-orbit (SO) splitting $\Delta_{SO} = \epsilon(\Gamma_8) - \epsilon(\Gamma_7)$ for all diamond-like group IV and zinc-blende group III-V, II-VI, and I-VII semiconductors using the full potential linearized augmented plane wave method within the local density approximation. The SO coupling is included using the second variation procedure, including the $p_{1/2}$ local orbitals. The calculated SO splittings are in very good agreement with available experimental data. The corrections due to the inclusion of the $p_{1/2}$ local orbital are negligible for lighter atoms, but can be as large as $\sim 250$ meV for $6p$ anions. We find that (i) the SO splittings increase monotonically when anion atomic number increases; (ii) the SO splittings increase with the cation atomic number when the compound is more ionic such as in III-V compounds; (iii) the SO splittings decrease with the cation atomic number when the compound is more ionic, such as in II-VI and the III-nitride compounds; (iv) the common-anion rule, which states that the variation of $\Delta_{SO}$ is small for common-anion systems, is usually obeyed, especially for ionic systems, but can break down if the compounds contain second-row elements such as BSe; (v) for IB-VII compounds, the $\Delta_{SO}$ is small and in many cases negative and it does not follow the rules discussed above. These trends are explained in terms of atomic SO splitting, volume deformation-induced charge renormalization, and cation-anion $p-d$ couplings.

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I. INTRODUCTION

Spin-orbit (SO) splitting $\Delta_{SO} = \epsilon(\Gamma_8) - \epsilon(\Gamma_7)$ at the top of the valence band of a semiconductor is an important parameter for the determination of optical transitions in these systems. It is also an important parameter to gauge the chemical environment and bonding of a semiconductor. Extensive studies of SO splitting, both theoretically and experimentally, have been carried out in the past. However, most of these studies focussed on a specific compound or a small group of similar compounds. Therefore, the general trends of the spin-orbit splitting in zinc-blende semiconductors is not very well established. From the experimental point of view, some of the data were measured more than 30 years ago and the accuracy of these data is still under debate. For example, previous experimental data suggest that CdTe and HgTe have SO splittings $\Delta_{SO}$ at about 0.8 and 1.08 eV, respectively. These values have been used widely by experimental groups to interpret optical and magneto-optical transition data of CdTe, HgTe, and related alloys and heterostructures. However, recent experimental data suggest that $\Delta_{SO}$ for CdTe and HgTe are instead around 0.95 eV and 0.91 eV. Without basic understanding of the general trends of variation of $\Delta_{SO}$ in tetrahedral semiconductors, it is difficult to judge what should be the correct value of $\Delta_{SO}$ for CdTe and HgTe. There are also several non-conventional II-VI and III-V semiconductors that do not have a zinc-blende ground state (e.g., CdO, MgO, GaBi, InBi), but that do form zinc-blende alloys with other compounds, and are currently under intensive research as novel opto-electronic materials. Therefore, it is important to know the spin-orbit splittings of these compounds in the zinc-blende phase and understand how they vary as a function of alloy concentration $x$ in the alloy.

From the theoretical point of view, various approximations have been used to calculate and/or predict SO splitting $\Delta_{SO}$. However, it is not clear how these approximations affect the calculated $\Delta_{SO}$. For example, one of the most widely used procedures for calculating the SO coupling using the density functional theory (DFT) and local density approximation (LDA) is the second-variation method used in many all-electron linearized augmented plane wave (LAPW) codes. In this approach, following the suggestion of Koelling and Harmon, the Hamiltonian of the relativistic Dirac equation is separated into a “$J$-weighted-averaged” scalar relativistic Hamiltonian $H_{SR}$, in which the dependancy on the quantum number $\kappa$ [where $\kappa = \pm(j + 1/2)$, with $j = l + s = l \mp 1/2$ is removed from the full Hamiltonian, and a spin-orbit Hamiltonian $H_{SO}$ with $H_{SO} = \frac{\hbar}{2Mc^2} \frac{1}{r} \frac{dV}{dr}(\tilde{l}, \tilde{s})$, where $M = m + \frac{\epsilon - V}{2c^2}$ is the relativistically enhanced electron mass, $c$ is the speed of light, $V$ is the effective potential, $\epsilon$ is the eigenvalue, and $\tilde{s}$ and $\tilde{l}$ are the Pauli spin and angular momentum operators, respectively. The scalar relativistic Hamiltonian, which includes the mass velocity and Darwin corrections, is solved first using standard diagonalization method for each spin orientation (or solved
FIG. 1: Comparison of $p_{1/2}$, $p_{3/2}$, and $p_{l=1}$ orbitals in atomic As and Bi showing the large discrepancy between $p_{1/2}$ and the $p_{l=1}$ orbitals, especially for the heavier Bi atom.

just once if the system is not spin polarized). The SO Hamiltonian is included subsequently, in where the full Hamiltonian is solved using the scalar relativistic wavefunctions as basis set. Normally, only a small number of scalar relativistic wavefunctions are included in the second step, and only the spherical part of the potential within a muffin-tin sphere centered on each atomic site is used in the SO Hamiltonian. The advantage of the second-variation method is the physical transparency (e.g., it keeps spin as a good quantum number as long as possible) and the efficiency, because, in most cases in the second step, only a small number of basis functions are needed to have good agreement with solutions of fully relativistic Dirac equations. This approach has been shown to obtain $\Delta_{SO}$ that is in excellent agreement with experiments. For example, the calculated $\Delta_{SO}$ for GaAs is 0.34 eV compared with experimental data of 0.34 eV.\[42\] Consequently, the SO splitting cannot be accurately evaluated, in general, with solely the $p_{l=1}$ orbital. However, no systematic studies have been done to evaluate the effect of the $p_{1/2}$ orbital on the calculated SO splitting $\Delta_{SO}$.

FIG. 2: Chemical trend of the spin-orbit splittings for all diamond-like group IV and zinc-blende group III-V, II-VI, and I-VII semiconductors, including the $p_{1/2}$ local orbitals. The graph corresponds to the data in column “LAPW+$p_{1/2}$” of Tables II, III, and IV.

FIG. 3: Atomic spin-orbit splittings $\epsilon(p_{3/2}) - \epsilon(p_{1/2})$ for atoms studied in this paper. The spin-orbit splittings increase as a function of the atomic number $Z$. See Table IV for data subdivided according to their respective groups.

The objective of this paper is to do a systematic study of the SO splitting $\Delta_{SO}$ of all diamond-group IV and zinc-blende groups III-V, II-VI, and I-VII semiconductors using the first-principles band-structure method within the density functional formalism. We find that the cal-

FIG. 1: $\psi(z)$ for (a) As $4p$ and (b) Bi $6p$. The inset shows the $p_{1/2}$ and $p_{3/2}$ orbitals as functions of the atomic number Z.

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culated SO splittings including the \( p_{1/2} \) local orbital are in good agreement with available experimental data. The general chemical trends of the \( \Delta_{SO} \) are revealed and explained in terms of atomic SO splittings, volume effects, and \( p-d \) coupling effects.

II. METHOD OF CALCULATIONS

The calculations are performed using the full potential linearized augmented plane wave (FLAPW) method as implemented in the WIEN2k code.\(^{40,42}\) The frozen core projector augmented wave (PAW) approach implemented in the VASP code\(^{34,35}\) is used for comparison. We used the Monkhost-Pack\(^{37} 4 \times 4 \times 4 \) \( k \) points for the Brillouin zone integration. For the FLAPW method, SO coupling is included using the second-variation method performed with or without the \( p_{1/2} \) local orbitals. Highly converged cutoff parameters in terms of the numbers of spherical harmonics inside the muffin-tin region and the plane waves in the interstitial region, as well as local orbitals for low-lying valence band states (anion \( s \) and cation \( d \) states), are used to ensure the full convergence of the calculated values. For the PAW method, high precision energy cutoffs have been chosen for all semiconductors (as large as 37 Rydberg for the nitrides and oxides).

In most cases, the band structure calculations are performed at the experimental lattice constants. For compounds that have only experimental lattice constant in the wurtzite structure, such as ZnO, we assume that zinc-blende ZnO has the same volume as in its wurtzite structure.\(^{16}\) For BSB, the (Al, Ga, In)Bi, and the (Be, Mg, Cd, Hg)O, that does not have either zinc-blende or wurtzite experimental structure parameters, the LDA-calculated lattice constants are used. For the silver halides and the gold halides, the LDA lattice constants have been corrected according to the small discrepancy between LDA and experimental values of AgI (more precisely, 0.088 Å have been added to the LDA lattice constants of silver halides and gold halides). The LDA-calculated lattice constants are expected to be reliable. For example, our predicted\(^{30} \) lattice constant of GaBi is \( a = 6.324 \) Å, whereas recent experimental observation\(^{21} \) finds a value around 6.33±0.06 Å, in good agreement with our prediction. All the lattice constants used in our calculation are listed in Tables II, III, and IV.

III. EFFECT OF THE \( p_{1/2} \) LOCAL ORBITAL

Tables II, III, and IV present the calculated SO splittings data for all diamond-like group IV and zinc-blende groups III-V, II-VI, and I-VII semiconductors. The calculated values are obtained with or without the \( p_{1/2} \) local orbitals. We find that including the \( p_{1/2} \) local orbital provides a better variation basis for the \( \Gamma_v \) state, lowers the eigen energy, and, therefore, increases the SO splitting

\[
\Delta_{SO} = \epsilon(\Gamma_{8v}) - \epsilon(\Gamma_{7v}).
\]

The correction due to the \( p_{1/2} \) orbital increases as the atomic number increases. Since the VBM consists of mostly anion \( p \) state, the dependence is more on anion atomic numbers. We find that corrections due to the inclusion of the \( p_{1/2} \) local orbital (for both anions and cations) are negligible for lighter atoms, are \( \sim 10 \) meV for \( 4p \) anions, \( \sim 40 \) meV for \( 5p \) anions and can be as large as \( \sim 250 \) meV for \( 6p \) anions. Thus, for Bi compounds (AlBi, GaBi, and InBi), large errors could be introduced if the \( p_{1/2} \) local orbital is not included.\(^{21} \) In all the cases, inclusion of \( p_{1/2} \) local orbital brings a better agreement between the calculated \( \Delta_{SO} \) and available

| Comp. | \( a \) (Å) | \( \Delta_{SO} \) [meV] |
|-------|------------|---------------------|
|       | LAPW | LAPW+\( p_{1/2} \) | PAW | exper. |
| IV    |       |                     |
| C     | 3.5668 | 13                  | 13  | 13\(^a\) |
| SiC   | 4.3596 | 14                  | 15  | 10\(^b\) |
| Si    | 5.4307 | 49                  | 50  | 44\(^c\) |
| Ge    | 5.6579 | 298                 | 302 | 302 296\(^b\) |
| α-Sn  | 6.4890 | 669                 | 697 | 689 800\(^e\) |
|       |       |                     |     |       |
| III-V |       |                     |
| BN    | 3.6157 | 21                  | 21  | 22   |
| BP    | 4.5383 | 41                  | 41  | 42   |
| BAs   | 4.7770 | 213                 | 216 | 212  |
| BSB   | 5.1982 | 348                 | 366 | 346  |
| AlN   | 4.3600 | 19                  | 19  | 19\(^d\) |
| AlP   | 5.4635 | 59                  | 59  | 62   |
| AlAs  | 5.6600 | 296                 | 300 | 275\(^b\), 300\(^c\) |
| AlSb  | 6.1355 | 658                 | 681 | 679 750\(^b\), 673\(^b\) |
| AlBi  | 6.3417 | 1 895               | 2 124 | 2 020  |
| GaN   | 4.5000 | 12                  | 12  | 11\(^c\), 17\(^d\) |
| GaP   | 5.4505 | 86                  | 86  | 88   |
| GaAs  | 5.6526 | 338                 | 342 | 342 341\(^e\) |
| GaSb  | 6.0951 | 714                 | 738 | 722 752\(^b\), 730\(^b\) |
| GaBi  | 6.3240 | 1 928               | 2 150 | 2 070  |
| InN   | 4.9800 | -1                  | 0   | 0    |
| InP   | 5.8687 | 100                 | 102 | 104 108\(^c\), 99\(^d\) |
| InAs  | 6.0583 | 344                 | 352 | 355 371\(^b\), 380\(^b\) |
| InSb  | 6.4794 | 731                 | 755 | 754 803\(^b\), 850\(^b\), 750\(^d\) |
| InBi  | 6.6860 | 1 917               | 2 150 | 2 089  |

\(^{a}\) Reference \(^{50}\)
\(^{b}\) Reference \(^{17}\)
\(^{c}\) Reference \(^{30}\)
\(^{d}\) Reference \(^{31}\)
\(^{e}\) Reference \(^{21}\)
\(^{f}\) Reference \(^{21}\)
\(^{g}\) Reference \(^{21}\)
IV. CHEMICAL TRENDS

Figure 2 shows the general chemical trends of the calculated SO splittings $\Delta_{SO}$ for all diamond-like group IV and zinc-blende III-V, II-VI, and I-VII semiconductors, with inclusion of the $p_{1/2}$ local orbitals. We find that (i) the SO splittings increase monotonically when anion atomic number increases; (ii) the SO splittings increase with the cation atomic number when the compound is more ionic, such as in II-VI and the III-nitride compounds; (iii) the SO splittings decrease with the cation atomic number when the compound is more ionic, such as in II-VI and their LDA energy minimum (for ZnO $\star\star$), the lattice constant of the zinc-blende structure is chosen so that its volume is equal to that in the wurtzite structure). Our results are compared with available experimental data. Our error analysis suggests that due to the overestimation of the $p$-$d$ hybridization, our calculated $\Delta_{SO}$ is underestimated by 30, 40, and 110 meV for Zn, Cd, and Hg compounds, respectively. For other compounds, the LDA error is estimated to be less than 20 meV.

| Comp. | $a$ (Å) | $\Delta_{SO}$ [meV] |
|-------|---------|---------------------|
|       | LAPW   | LAPW+$p_{1/2}$ | PAW | exper. |

| II-A-VI |       |       |       |       |       |
|---------|-------|-------|-------|-------|-------|
| BeO     | 3.7654 | 36    | 36    | 38    | —     |
| BeS     | 4.8650 | 98    | 98    | 98    | —     |
| BeSe    | 5.1390 | 445   | 449   | 447   | —     |
| BeTe    | 5.6250 | 927   | 965   | 944   | —     |
| MgO     | 4.5236 | 34    | 34    | 34    | —     |
| MgS     | 5.6220 | 87    | 87    | 87    | —     |
| MgSe    | 5.8900 | 396   | 399   | 396   | —     |
| MgTe    | 6.4140 | 832   | 869   | 854   | 945   |
| HgO     | 5.1566 | -285  | -281  | -292  | —     |
| HgS     | 5.8500 | -100  | -87   | -108  | —     |
| HgSe    | 6.0850 | 235   | 254   | 238   | 450$^e$, 396$^d$, 300$^g$ |
| HgTe    | 6.4603 | 762   | 800   | 781   | 1080$^f$, 910$^g$ |

| II-B-VI |       |       |       |       |       |
|---------|-------|-------|-------|-------|-------|
| ZnO     | 4.5720$^\star\star$ | -34   | -34   | -37   | -4$^b$ |
| ZnS     | 5.4102 | 66    | 66    | 64    | 65$^c$, 86$^d$ |
| ZnSe    | 5.6676 | 393   | 398   | 392   | 420$^e$, 400$^d$ |
| ZnTe    | 6.0890 | 889   | 916   | 898   | 910$^e$, 950$^a$ |
| CdO     | 5.0162$^*$ | -59   | -60   | -58   | —     |
| CdS     | 5.8180 | 50    | 50    | 46    | 62$^c$, 56$^b$ |
| CdSe    | 6.0520 | 364   | 369   | 370   | 416$^d$, 390$^e$ |
| CdTe    | 6.4820 | 848   | 880   | 865   | 810$^c$, 800$^f$, 900$^f$ |
| HgO     | 5.1566$^*$ | -285  | -281  | -292  | —     |
| HgS     | 5.8500 | -100  | -87   | -108  | —     |
| HgSe    | 6.0850 | 235   | 254   | 238   | 450$^e$, 396$^d$, 300$^g$ |
| HgTe    | 6.4603 | 762   | 800   | 781   | 1080$^f$, 910$^g$ |

$^a$ Reference 26.  
$^b$ Reference 25.  
$^c$ Reference 24.  
$^d$ Reference 23.  
$^e$ Reference 22.  
$^f$ Reference 21.  
$^g$ Reference 20.  

The experimental data.

$\Delta_{SO}(p_{3/2} - p_{1/2}) \propto Z^\alpha$, where $\alpha$ is close to 2. (b) Dependence on the volume. As the volume of the compound decreases, the charge distribution in the crystal is renormalized. The bonds become more covalent. More charge is pushed into a region near the nuclei. Because the SO coupling is larger near the nuclear site, the SO splitting $\Delta_{SO}$ usually increases as the volume decreases. (c) Dependence on the cation valence $d$ orbital. The VBM in a majority of zinc-blende semiconductors consists of mostly anion $p$ and a smaller amount of cation $p$ orbitals. By symmetry, the VBM state in zinc-blende
structure can couple with the cation $t_{2d}$ orbitals. The cation $t_{2d}$ orbital has a negative contribution\(^{1,15}\) to the SO splitting $\Delta_{SO}$ (i.e., the $\Gamma_{8v}$ is below the $\Gamma_{7v}$ state). Thus, large mixing of heavy cation $d$ orbitals in VBM can reduce $\Delta_{SO}$.

Using the discussion above, we can now understand the general chemical trends of the SO splitting $\Delta_{SO}$.  

(i) The SO splittings increase monotonically when anion atomic number increases. For example, $\Delta_{SO}$ increases from $13 \rightarrow 49 \rightarrow 302 \rightarrow 697$ meV when the atomic number increases from C $\rightarrow$ Si $\rightarrow$ Ge $\rightarrow$ $\alpha$-Sn; from $12 \rightarrow 86 \rightarrow 342 \rightarrow 2150$ meV when the anion atomic number increases from GaN $\rightarrow$ GaP $\rightarrow$ GaAs $\rightarrow$ GaSb $\rightarrow$ GaBi; from $-60 \rightarrow 50 \rightarrow 369 \rightarrow 880$ meV when the anion atomic number increases from CdO $\rightarrow$ CdS $\rightarrow$ CdSe $\rightarrow$ CdTe; from $-85 \rightarrow 82 \rightarrow 455$ when the anion atomic number increases from CuCl $\rightarrow$ CuBr $\rightarrow$ CuI. This is because the VBM has large anion $p$ character, and the atomic SO splitting of the anion valence $p$ state increases with the atomic number (see Table IV). One of the interesting case is SiC. The calculated $\Delta_{SO}$ of 14 meV for SiC is very close to the one of diamond (13 meV), indicating that SiC is a very ionic material with its VBM containing mostly C character. Figure 4 depicts the contour plot of the charge distribution at the VBM for SiC, which shows that the VBM charge is located on the carbon atom site.

(ii) The SO splittings increase with the cation atomic number when the compound is more covalent, such as in most III-V compounds. For example, $\Delta_{SO}$ increases from $216 \rightarrow 300 \rightarrow 342 \rightarrow 352$ meV when the atomic number increases from BAs $\rightarrow$ AlAs $\rightarrow$ GaAs $\rightarrow$ InAs; from $366 \rightarrow 681 \rightarrow 738 \rightarrow 755$ meV when the atomic number increases from BSb $\rightarrow$ AlSb $\rightarrow$ GaSb $\rightarrow$ InSb. This is because for covalent III-V compounds, the VBM contains significant amount of cation $p$ orbitals. Therefore, when the cation atomic number increases, the SO splitting $\Delta_{SO}$ also increases. It is interesting to note that $\Delta_{SO}$ for BX (X=P, As, and Sb) is significantly smaller than that for their corresponding common-anion compounds. For example, $\Delta_{SO}$(BSb)=366 meV is only about half of the value of $\Delta_{SO}$(GaSb)=738 meV. This is because boron is much more electronegative than other group III elements. Thus, BX compounds are much more covalent than the other III-V semiconductors. Figure 5 compares the charge distribution of the VBM states for BSb and GaSb. We see that for GaSb, most of the VBM charge is on Sb atom site, whereas for BSb, a large portion of the

![FIG. 5: Charge density of the VBM state for GaSb and BSb, showing that for BSb the role of cation and anion is reversed.](image)

TABLE III: Calculated spin-orbit splitting $\Delta_{SO}$ for all IB-VII compounds, using the FLAPW method, with or without the $p_{1/2}$ local orbitals, and the frozen-core PAW method. Our results are compared with available experimental data. We use experimental lattice constants\(^{48,52,53}\) for CuX (X= Cl, Br, I) and AgI. The lattice constants for the other AgX and AuX compounds are estimated from calculated LDA lattice constants and experimental lattice constant of AgI. Due to the overestimation of the $d$ character in the VBM, the LDA underestimate the $\Delta_{SO}$ by 20, 60, and 170 meV for chlorides, bromides, and iodides, respectively.

| Compound | $a$ (Å) | $\Delta_{SO}$ [meV] |
|----------|--------|---------------------|
|          | LAPW   | LAPW+$p_{1/2}$ | PAW | exper. |
| IB-VII   |        |                    |     |        |
| CuCl     | 5.4057 | -85                | -85 | -69\(^a\) |
| CuBr     | 5.6905 | 80                 | 82  | 86     | 147\(^a\) |
| CuI      | 6.0427 | 440                | 455 | 466    | 633\(^a\) |
| AgCl     | 5.8893 | -119               | -118| -122   |        |
| AgBr     | 6.1520 | 155                | 157 | 158    |        |
| AgI      | 6.4730 | 643                | 664 | 658    | 837\(^a\) |
| AuCl     | 5.7921 | -444               | -444| -446   |        |
| AuBr     | 6.0517 | -177               | -173| -178   |        |
| AuI      | 6.3427 | 294                | 317 | 317    |        |

\(^a\) References 54 and 55.
FIG. 6: Charge density of the VBM states for Ge, GaAs, ZnSe, and CuBr showing that as ionicity increases, the charge is more localized on the anion site. For ZnSe and CuBr, it also shows antibonding $d$ character on the Zn and Cu sites, respectively.

VBM charge is on the B atom site. Because boron has a small atomic number ($Z=5$), the SO splitting of B 2$p$ states is very small, leading to very small $\Delta_{SO}$ for BX. This indicates that the common-anion rule, which states that the variation of $\Delta_{SO}$ is small for common anion systems, does not apply to all BX, which are extremely covalent.

(iii) The SO splittings decrease with the cation atomic number when the compound is more ionic, such as in II-VI and III-nitride compounds. For example, $\Delta_{SO}$ decreases from 449 $\rightarrow$ 399 meV when the atomic number increases from BeSe $\rightarrow$ MgSe; from 965 $\rightarrow$ 869 meV when the atomic number increases from BeTe $\rightarrow$ MgTe; from 398 $\rightarrow$ 369 $\rightarrow$ 254 meV when the atomic number increases from ZnSe $\rightarrow$ CdSe $\rightarrow$ HgSe; from 21 $\rightarrow$ 19 $\rightarrow$ 12 $\rightarrow$ 0 meV when the atomic number increases from BN to AlN $\rightarrow$ GaN $\rightarrow$ InN. This is because for ionic II-VI and III-nitride systems, the VBM is mostly an anion $p$ state, thus the $\Delta_{SO}$ is not sensitive to the cation atomic number or potential. However, when cation atomic number decreases, say from Mg to Be, the volume of the compounds decreases (Table II), and therefore, due to the charge renormalization effect, the $\Delta_{SO}$ increases. In particular, for the IIB-VI systems and the III-nitrides, the coupling between cation $d$ and anion $p$ also plays an important role in the observed trend, because the $p$-$d$ hybridization is significant in these systems (See Fig. 6). The $p$-$d$ hybridization reduces $\Delta_{SO}$ and the effect increases when cation atomic number increases. This explains why $\Delta_{SO}$(HgX) (for X=O, S, Se, Te) is smaller than $\Delta_{SO}$(CdX), even though they have similar volume, and why $\Delta_{SO}$(InN) is smaller than $\Delta_{SO}$(GaN). Note that negative $\Delta_{SO}$ can exist in some of the compounds such as ZnO, CdO, and HgO where the anion is light, so their $p$ orbitals have only a small contribution to $\Delta_{SO}$, but the negative contribution of the cation $d$ orbital is large.

(iv) For compounds with the same principal quantum number $n$, $\Delta_{SO}$ increases as the ionicity of the compound increases. For example, for $n=2$, from C $\rightarrow$ BN $\rightarrow$ BeO, the SO splittings $\Delta_{SO}$ increase from 13 $\rightarrow$ 21 $\rightarrow$ 36 meV; for $n=3$, from Si $\rightarrow$ AlP $\rightarrow$ MgS, the SO splittings increase from 49 $\rightarrow$ 59 $\rightarrow$ 87 meV; for $n=4$, from Ge $\rightarrow$ GaAs $\rightarrow$ ZnSe, the SO splittings increase from 302 $\rightarrow$ 342 $\rightarrow$ 398 meV; for $n=5$, from $\alpha$-Sn $\rightarrow$ InSb $\rightarrow$ CdTe, the SO splittings increase from 697 $\rightarrow$ 755 $\rightarrow$ 880 meV. The reason for this increase can be understood from plots in Fig. 6 which show the charge distribution of the VBM states of Ge, GaAs, and ZnSe.

TABLE IV: Atomic SO splitting $\epsilon(p_{3/2}) - \epsilon(p_{1/2})$ for the compounds of Tables I, II, and III according to their atomic groups. The data are also depicted in Fig. 3 as a function of atomic numbers $Z$.

| element | atomic number | $\epsilon(p_{3/2}) - \epsilon(p_{1/2})$ [meV] |
|---------|---------------|------------------------------------------|
| IB      |               |                                          |
| Cu      | Z=29         | 41                                       |
| Ag      | Z=47         | 133                                      |
| Au      | Z=79         | 569                                      |
| II A    |               |                                          |
| Be      | Z=4          | 1                                        |
| Mg      | Z=12         | 7                                        |
| III     |               |                                          |
| Zn      | Z=30         | 67                                       |
| Cd      | Z=48         | 196                                      |
| Hg      | Z=80         | 732                                      |
| III I   |               |                                          |
| B       | Z=5          | 3                                        |
| Al      | Z=13         | 17                                       |
| Ga      | Z=31         | 121                                      |
| In      | Z=49         | 314                                      |
| IV      |               |                                          |
| N       | Z=7          | 19                                       |
| P       | Z=15         | 55                                       |
| As      | Z=33         | 282                                      |
| Sb      | Z=51         | 632                                      |
| Bi      | Z=83         | 1 968                                    |
| VI      |               |                                          |
| O       | Z=8          | 37                                       |
| S       | Z=16         | 86                                       |
| Se      | Z=34         | 386                                      |
| Te      | Z=52         | 815                                      |
| VII     |               |                                          |
| Cl      | Z=17         | 127                                      |
| Br      | Z=35         | 509                                      |
| I       | Z=53         | 1 029                                    |

and why $\Delta_{SO}$(InN) is smaller than $\Delta_{SO}$(GaN). Note that negative $\Delta_{SO}$ can exist in some of the compounds such as ZnO, CdO, and HgO where the anion is light, so their $p$ orbitals have only a small contribution to $\Delta_{SO}$, but the negative contribution of the cation $d$ orbital is large.
As the system changes from group IV → III-V → II-VI, the compound becomes more ionic and the VBM becomes more localized on the anion site with increasing atomic number, thus $\Delta_{SO}$ increases. It is interesting to note that the differences of $\Delta_{SO}$ between the II-VI, the III-V, and the group IV compounds in the same row increases as $n$ increases (almost doubles when $n$ increases by one). This is explained by the fact that the atomic number $Z$ almost doubles when $n$ is increased by one, whereas the atomic SO splitting is proportional to $Z^n$ with $\alpha$ close to 2 (See Table IV and the discussion above); thus, the difference is proportional to $Z$.

(v) The $A^{IB}X^{VII}$ halides ($A^{IB} = Cu$, Ag, Au; $X^{VII} = Cl, Br, I$) constitute a group of special compounds that do not follow the rules discussed above. For example, when moving from ZnSe to CuBr with increased ionicity (see Figure 6), the SO splitting of CuBr (82 meV) is much smaller than that for ZnSe (398 meV). The SO splitting of AgI (664 meV) is also much smaller than that of CdTe (880 meV). Furthermore, many of the IB-VII compounds (CuCl, AgCl, AuCl, and CuBr) have negative SO splittings, and for these ionic compounds CuX$^{VII}$ has much smaller SO splittings than AgX$^{VII}$ and AuX$^{VII}$. The origin of these anomalies is due to the fact that for most of the IB-VII compounds the VBM is no longer an anion $p$ dominated state. Instead, they are cation $d$ states strongly hybridized with the anion $p$ state. For instance, in Figure 6(d) we show that the VBM of CuBr has a very pronounced antibonding $d$ character at the cation Cu site. Because the $d$ state has negative $\Delta_{SO}$, this explains why some of the IB-VII compounds have negative $\Delta_{SO}$. Furthermore, because Cu 3$d$ level is much higher than Ag 4$d$ and Au 5$d$ levels, the VBM of Cu halides contains more cation $d$ character than Ag and Au compounds. This explains why Cu halides have much smaller $\Delta_{SO}$ than the Ag and Au common anion halides.

V. COMPARISON WITH EXPERIMENTS

Our calculated results with the $p_{1/2}$ local orbitals are compared with experimental data.\cite{16,17,18,19,20,21,22,23,24,25,26,27,28,29,30} For most semiconductors the agreement is very good. For example, the calculated value for diamond (13 meV) is in very good agreement with the recently experimentally derived value of 13 meV.\cite{50} The experimental value for SiC in the zinc-blende structure (10 meV)\cite{15} is smaller than the one for C, therefore, does not follow the chemical trend. We suggest that the measured value is possibly underestimated. For most semiconductors, the difference between theory and experiment is usually less than 20 meV. However, there are several noticeable cases in which the difference is much larger. For example, for $\alpha$-Sn, the calculated value is 697 meV, whereas the value in experiment data\cite{16} is $\sim$800 meV. For HgTe the calculated value at 800 meV is much smaller than the widely used experimental value\cite{15} of 1080 meV. To understand the origin of the discrepancy, we performed the following tests. First, we considered a different numerical approach, i.e., the frozen core PAW method as implemented in the VASP code to calculate the SO splitting $\Delta_{SO}$. Despite the large difference in the way the SO coupling is implemented in the calculations, we find that the $\Delta_{SO}$ calculated with the PAW method are very similar to that obtained with the FLAPW method. For $\alpha$-Sn and HgTe, the results obtained by the PAW method are 689 and 781 meV, respectively, in good agreement with the FLAPW-calculated values of 697 and 800 meV. Next, we estimated the effect of $p$-$d$ coupling. It has been argued that the LDA-calculated cation $d$ orbitals are too shallow so $p$-$d$ hybridization at the VBM is overestimated, which may lead to smaller calculated $\Delta_{SO}$. To verify if this is the possible reason, we performed the following calculations. (i) After obtaining the converged LDA potential, we removed the cation orbital from the basis set to calculate the $\Delta_{SO}$. We find that for $\alpha$-Sn, this procedure has no effect on the calculated $\Delta_{SO}$. This is consistent with the fact that for this compound, the cation $d$ and anion $p$ separation is large enough that the amount of cation $d$ orbital at the VBM is not sufficient to affect the calculated $\Delta_{SO}$. For ZnTe, CdTe, and HgTe, removing the cation orbital increases the $\Delta_{SO}$ by 48, 63, and 253 meV, respectively. These values are the upper limit on the possible effect of $p$-$d$ coupling on the calculated $\Delta_{SO}$. (ii) To get more reliable estimates on the LDA error of the calculated $\Delta_{SO}$, we added an external potential\cite{51} on the cation muffin-tin sphere to push down the cation $d$ orbitals such that the calculated cation binding energy is close to the experimental photemission data.\cite{22} In this case, the calculated $\Delta_{SO}$ is 0.94, 0.91, and 0.90 eV for ZnTe, CdTe, and HgTe, respectively. The above analysis demonstrates that the possible LDA error in calculating $\Delta_{SO}$ is less than 30, 40, and 110 meV for Zn, Cd, and Hg compounds, respectively, and much smaller for other compounds.

Our analysis above suggests that $\Delta_{SO}$ for $\alpha$-Sn and HgTe should be around 0.70 and 0.90 eV, respectively, smaller than the experimental values of 0.80 and 1.08 eV, respectively. The origin of this discrepancy is still not very clear. But we notice that $\alpha$-Sn and HgTe are semimetals, i.e., the $\Gamma_{6c}$ state is below the VBM. This makes the accurate measurement of the $\Delta_{SO}$ for these compounds more challenging. Indeed, recent measurements\cite{26} of $\Delta_{SO}$ for HgTe show that it has a value of 0.9 eV, in good agreement with our predicted value. We also notice that the recent reported experimental SO splitting for InSb\cite{21} which has a very small band gap (0.24 eV), agrees well with our calculation. Further experimental studies are needed to clarify these issues.
VI. SUMMARY

In summary, we have studied systematically the SO splitting $\Delta_{SO}$ of all diamond-like group IV and zincblende group III-V, II-VI, and I-VII semiconductors using the first-principles band structure method. We studied the effect of the $p_{1/2}$ local orbitals on the calculated $\Delta_{SO}$. The general trends of $\Delta_{SO}$ of the semiconductors are revealed and explained in terms of atomic SO splitting, volume deformation-induced charge renormalization, and cation-anion $p-d$ couplings. In most cases, our calculated results are in good agreement with the experimental data. The differences between our calculated value for $\alpha$-Sn and HgTe, and to a lesser degree for InAs and GaSb, are highlighted. Experiments are called for to test our predictions.

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