Band gap of Hg chalcogenides: Symmetry-reduction-induced band-gap opening of materials with inverted band structures

Chang-Youn Moon and Su-Huai Wei

National Renewable Energy Laboratory, Golden, Colorado 80401, USA

We have investigated the band structure of zinc-blende (ZB) Hg chalcogenides using a corrected local density approximation method. We find that the band gaps of HgS, HgSe, and HgTe are 0.30, −0.24, and −0.31 eV, respectively. That is, HgS has a positive band gap, whereas HgSe and HgTe have inverted band structures. The chemical trend of the band gaps is explained by the atomic energy levels and sizes, as well as by the related deformation potentials for these compounds. We also show systematically how the band gap of the inverted band structure can open up when the T_d symmetry of the ZB structure is reduced under strain or in the presence of a surface or interface.

I. INTRODUCTION

The band gap of a semiconductor is one of the most important parameters that affects its electrical, optical, and magnetic properties. The band gaps of most III-V and II-VI compounds have been accurately measured and given in various reference books.[1] However, the band gaps for some of these compounds have recently become the subject of debate. One of the famous examples is InN. Previous experimental measurement suggested that the band gap of InN is about 1.9 eV,[2] but recent experimental measurements[3,4] and theoretical calculations[5,6] find that, for bulk stoichiometric InN, the intrinsic band gap should be around 0.7 eV. Another example is the mercury chalcogenides Hg*X* (*X*=S, Se, Te) in the zinc-blende (ZB) structure. For several decades, it was believed[1] that Hg chalcogenides belong to a group of unique materials exhibiting the so-called inverted band structure.[7] In this band structure, the energy of the *s*-like Γ_6 state, which is the conduction-band minimum (CBM) at Γ for most ZB semiconductors, is below the *p*-like valence-band maximum (VBM) with the Γ_8 symmetry. Subsequently, due to the degeneracy of the Γ_8 state, the CBM and VBM touch each other at the Γ point; hence the band gap is exactly equal to zero (Fig. 1), which is semimetallic. Because the state with the Γ_6 symmetry is now below the Γ_8 state, these materials are sometimes also called "negative-band-gap" materials. However, this point of view was challenged by Gawlik *et al.*[8] Using a combination of angle-resolved photoemission and inverse photoemission measurements, they showed that *n*-type HgSe(100) has a positive band gap of 0.42 eV. This discovery has stimulated many new investigations about the nature of the band structures of Hg chalcogenides. Most subsequent experiments using different techniques,[9–11] however, suggest that HgSe has a semimetallic nature, which is also supported by another photoemission experiment[12] as well as first-principles local density approximation (LDA) and *GW* quasiparticle calculations.[13–15]

Another interesting theoretical issue for the Hg chalcogenides is that the reported band gaps for HgS, HgSe, and HgTe are nearly the same, around −0.25 eV.[1,16] This is quite surprising because for Zn and Cd chalcogenides the band gaps decrease when anion atomic number increases. For ex-

ample, for Zn compounds, the band gap is 3.8, 2.8, and 2.4 eV for ZnS, ZnSe, and ZnTe, respectively; and for Cd compounds, they are 2.6, 1.9, and 1.6 eV for CdS, CdSe, and CdTe, respectively.[1] In a recent theoretical study,[15] it was suggested that HgS may have a positive band gap equal to the spin-orbit (SO) splitting of the Γ_{15v} state,[15] because HgS has a negative spin-orbit coupling,[17] so the doubly degenerate empty Γ_7 state is above the fourfold-degenerate fully occupied Γ_8 state, even though the Γ_6 level is below the Γ_8 level.

In this paper, we calculate the band gaps of Hg chalcogenides using a corrected local density approximation method.[6] We find that the band gaps of HgS, HgSe, and HgTe are 0.30, −0.24, and −0.31 eV, respectively. That is, for HgS, there is a positive band gap with Γ_6 as the CBM, whereas for HgSe and HgTe, the Γ_6 level is below the Γ_8 VBM state. The chemical trend of the band gaps is explained by the atomic energy levels and size, as well as by the related deformation potentials for these compounds.[18] We also show that the degenerate Γ_8 state of the inverted band materials (HgSe and HgTe) could split and open a small band gap when the T_d symmetry of the ZB structure is reduced under strain or in the presence of a surface or interface. Hence, it provides a partial explanation to the puzzling experimental result of Gawlik *et al.*, who found that the band gap of HgSe (001) is positive.[8]
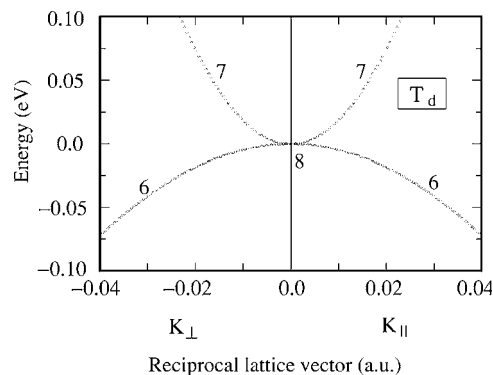

FIG. 1. The inverted band structure of a ZB crystal with T_d symmetry. $K_\perp$ is along the [001] direction and $K_\parallel$ is along the [100] direction.

045205-1

II. METHOD OF CALCULATIONS

The band structure calculations in this study are performed using the fully relativistic (including spin-orbit coupling), general potential, linearized augmented plane wave method[19] at experimental lattice constants.[1] The absorption coefficients are calculated using the optical package in WIEN2K.[20] It is well known that the first-principles LDA calculation severely underestimates the semiconductor band gap.[6,15] Direct first-principles calculations using the more complex *GW* approach for Hg compounds is currently also problematic due to the presence of Hg *d* orbitals and the negative band gap for these compounds.[5,13,14] To overcome these problems, we have used a well-established semiempirical approach[6] to correct the LDA band gap error by adding to the LDA potential a δ-function-like external potential[6,21] inside the muffin-tin spheres centered at each atomic site α,

$$V_{ext}^{\alpha}(r) = \bar{V}^{\alpha} + V_0^{\alpha}\left(\frac{r_0^{\alpha}}{r}\right)e^{-(r/r_0^{\alpha})^2}, \qquad (1)$$

and performed the calculation self-consistently. Specifically, the parameters in Eq. (1) are fitted first only to the available experimental energy levels at high-symmetry *k* points for ZnTe, CdTe, and HgTe.[1] The same parameters are then used to predict the band gaps of selenides and sulfides. For Zn and Cd compounds, the predicted band gaps usually differ from experimental band gaps by less than 0.1 eV. This approach has also been used in the past to correctly predict the band gaps of III-V semiconductors such as InN with similar accuracy.[6] Based on these observations, we estimate that our predicted band gaps for HgS and HgSe are accurate within 0.1 eV. A more detailed description of these calculations will be given elsewhere.[22]

III. BAND GAP OF MERCURY CHALCOGENIDES IN ZB STRUCTURE: CHEMICAL TREND

Using this approach, our predicted band gaps for HgS, HgSe, and HgTe are 0.30, −0.24, and −0.31 eV, respectively. For HgSe and HgTe, the ordering is Γ_8-Γ_6-Γ_7, whereas for HgS, the ordering of the three band edge states is Γ_6-Γ_7-Γ_8. The order of the Γ_7 and Γ_8 states of HgS depends on the sign of the SO splitting, which depends on the exact position of the Hg 5*d* state inside the valence bands. Because after including the final-state effects the *d* orbital position is consistent with experimental photoemission data,[23] we used here the LDA calculated result, i.e., the SO splitting of HgS is small, but negative.[17] Our results show that (1) the band gaps of HgSe and HgTe are negative and have similar values, and (2) the band gap of HgS is positive and is much larger than those of HgSe and HgTe. To understand this, we notice that the Γ_6 state is an anion *s* and cation *s* state, whereas Γ_8 has mostly anion *p*, cation *p*, and cation *d* characters.[24] Because the Te 5*s* atomic orbital energy is about 2.1 eV higher than Se 4*s* orbitals,[18] if Se and Te were the same size, the CBM of the tellurides would be much higher than that of the corresponding selenides. The reason that ZnTe has a smaller band gap than ZnSe is because the Se 4*p* atomic orbital is about 0.5 eV lower than the Te 5*p* orbital, and because Se has a

smaller atomic size than Te. When volume decreases, the bonding Γ_8 state moves down in energy, whereas the antibonding Γ_6 state moves up in energy, increasing the band gap.[18] Therefore, the Γ_8 energy level of selenides is lower than that of tellurides. However, due to the large anion *p*–cation *d* repulsion in the Hg compounds, the VBM offset between HgSe and HgTe is smaller than between ZnSe and ZnTe.[25] Furthermore, due to the large anion-cation bond length, the magnitude of the CBM deformation potential for Hg compounds is also small.[18] Consequently, the band-gap difference between HgSe and HgTe is small, less than 0.1 eV, whereas for ZnSe and ZnTe, the difference is about 0.4 eV. Because the S 3*s* atomic orbital is 0.2 eV higher than the Se 4*s* orbital, and its 3*p* orbital energy is 0.45 eV lower than the Se 4*p* orbital, and, moreover, S is smaller than Se, there is no cancellation of the chemical and size effects between sulfides and selenides, so the band gap of sulfides should always be significantly larger than that of selenides. This analysis is consistent with the fact that the band gap of ZnS is 1.0 eV larger than that of ZnSe and the band gap of CdS is 0.7 eV larger than that of CdSe,[1] and also with our calculated result that the band gap of HgS is about 0.5 eV larger than that of HgSe.

Our calculated results are consistent with most experimental results[1,12,26] that show HgSe and HgTe have inverted band structures. Our prediction that ZB HgS has a positive band gap of 0.30 eV is also consistent with a recent *GW* calculation of Fleszar and Hanke.[14] They find that without including the spin-orbit coupling, the Γ_{1c} state is about 0.03 eV above the Γ_{15v} state. After including the spin-orbit coupling and correction for systematic errors of 0.3–0.6 eV underestimation of the band gap, the predicted band gap from the *GW* calculation should be around 0.25–0.55 eV. However, it does not agree with early experimental measurements,[1,16,27] which suggest that HgS also has a negative band gap. However, unlike HgSe and HgTe with the ZB ground state, the most stable crystal structure for HgS is the cinnabar structure, and, therefore, it is possible that early experimental samples contain some structural defects that closed the band gap. More experimental studies for this interesting material are needed to clarify this issue.

IV. BAND-GAP OPENING BY REDUCED CRYSTAL SYMMETRY

Our calculation for bulk ZB HgSe also does not support the conclusion of Gawlik *et al.*[8] that HgSe is a semiconductor. However, it is interesting to notice that the measurement of Gawlik *et al.* was performed on an *n*-type HgSe(001) surface with a $c(2 \times 2)$ reconstruction. Because the zero band gap of a semimetallic material is caused by the degeneracy of the Γ_8 state due to the high symmetry of the ZB structure, the reduced symmetry at the HgSe(001) surface should have a significant effect on the band structure for this material.[28] In the following, we will perform a symmetry analysis and numerical calculations to show how the band structure near the Γ_8 band edge of an inverted band material splits and opens up a small band gap when the crystal symmetry is reduced. We want to point out that the band-gap opening mechanism
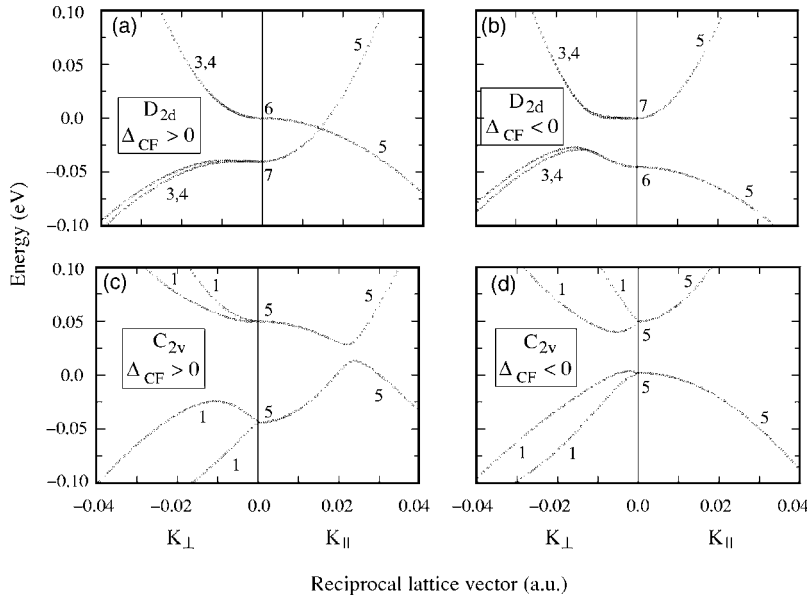
FIG. 2. The band structures for material with inverted band and reduced crystal symmetry of (a) D_{2d} and $\Delta_{CF}>0$, (b) D_{2d} and $\Delta_{CF}<0$, (c) C_{2v} and $\Delta_{CF}>0$, and (d) C_{2v} and $\Delta_{CF}<0$.

discussed here is different from that due to the upward shift of the Γ_6 state (e.g., under quantum confinement, hydrostatic pressure, or alloying with larger gap materials).[29]

A. T_d symmetry

When the crystal has the T_d symmetry of the ZB structure, the band structure of a semimetal is as shown in Fig. 1, where we plot band edge states along the [001] (denoted as $K_\parallel$) and [100] (denoted as $K_\perp$) directions. The k points on these two lines have the C_{2v} symmetry. In this case, the top of the valence band and the bottom of the conduction band merge at the Γ point, so the system has a zero band gap. Away from the Γ point, the fourfold-degenerate Γ_8 level splits into a twofold-degenerate Δ_{5c} conduction band and a Δ_{5v} valence band. The symmetries of the states are marked by the number shown in Fig. 1.

B. D_{2d} symmetry

When the ZB material is under a uniaxial strain along the [001] direction, the symmetry of the crystal is reduced from T_d to D_{2d}. With the lowered D_{2d} symmetry, the calculated band structures are shown in Figs. 2(a) and 2(b), corresponding to (a) positive and (b) negative crystal-field splittings Δ_{CF}. With positive Δ_{CF}, the doubly degenerate Γ_5 state [single group representation; see Fig. 3(b)] is above the Γ_4 state. They are both derived from the ZB Γ_{15} state at the VBM, and correspond to the situation when $c/a>1$, where c and a are lattice parameters along the [001] and [100] directions, respectively. When $c/a<1$, Δ_{CF} is negative. Under D_{2d} symmetry, the ZB Γ_8 state splits into Γ_6 and Γ_7 states. For positive Δ_{CF}, Γ_6 is above Γ_7, and for negative Δ_{CF}, Γ_6 is below Γ_7. Along the $K_\parallel$ direction, which has the C_{2v} symmetry, both bands are compatible with the Δ_5 symmetry. The band connected to the Γ_6 state moves down in energy and the one connected to the Γ_7 moves up in energy. Because states with the same symmetry cannot cross each other, there is a very small anticrossing gap in this direction when $\Delta_{CF}>0$.

When $\Delta_{CF}<0$, the band gap along this direction is proportional to the crystal-field splitting, and thus could be large. Along the $K_\perp$ direction, which now has a C_2 symmetry, both the Γ_6 and Γ_7 states are compatible with spin-split represen-
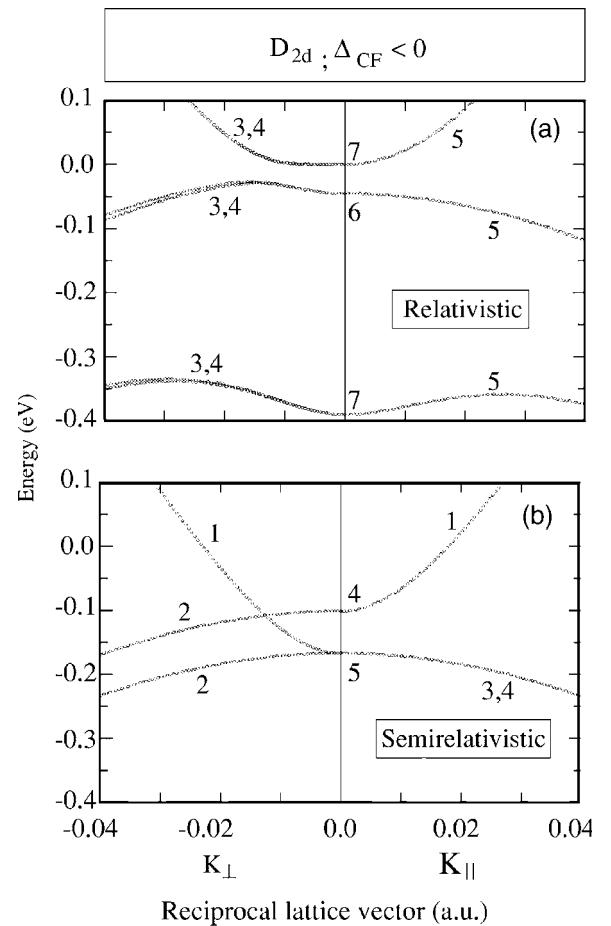

FIG. 3. The band structures for material with inverted band under reduced crystal symmetry of D_{2d} and $\Delta_{CF}<0$, (a) with and (b) without SO interaction.

tations 3 and 4. For $\Delta_{CF}>0$ case, the gap in this direction is proportional to the crystal-field splitting. For $\Delta_{CF}<0$, the anticrossing gap is significantly larger than that along the $K_{\parallel}$, which is due to its lower symmetry. This symmetry analysis indicates that under D_{2d} symmetry, if $\Delta_{CF}>0$, the VBM and CBM shift away from Γ, but the gap is near zero. However, if $\Delta_{CF}<0$, a band gap will open at a position away from Γ, and the system will no longer be a semimetal.

C. C_{2v} symmetry

As the crystal symmetry is further reduced to C_{2v}, which could be the situation in the presence of surface reconstruction or nonequivalent interfaces, the band structures are further modified. Figures 2(c) and 2(d) show the band structures and symmetries of the states. In this lowered symmetry, the anticrossing band gap along $K_{\parallel}$ increases when $\Delta_{CF}>0$. Along the $K_{\perp}$ direction, the symmetry is reduced to C_1. When $\Delta_{CF}<0$, the anticrossing band gap along this direction is quite large, similar to the crystal-field splitting gap at Γ.

D. Effect of SO interaction

Here we should point out that the band-gap opening is a combined effect of symmetry lowering caused by strain or formation of surface and the SO coupling, because SO coupling further reduces the crystal symmetry. To demonstrate this, we show in Fig. 3 the band structure of a system with D_{2d} crystal symmetry and negative Δ_{CF}. When the SO coupling is neglected, the band structure is as shown in Fig. 3(b), where each band is spin degenerate and single group notation is used. In this case, the triply degenerate Γ_{15} states in T_d symmetry split into singly degenerate Γ_4 and doubly degenerate Γ_5 states. Along the $K_{\perp}$ direction, the Γ_5 state splits into two states with representations 1 and 2. The band with symmetry 1 can cross the band with symmetry 2 which is compatible with the high-lying Γ_4 state, so no band gap exists. When the SO coupling is included, the symmetry of the states along $K_{\perp}$ can only have representations 3 and 4, which split very little as shown in Fig. 3(a); therefore, an anticrossing band gap appears.

E. Numerical test

To show quantitatively the size of the symmetry-reduction-induced band gap, we have calculated the band gap of HgSe under biaxial tensile strain, that is, the system has a D_{2d} crystal symmetry and negative Δ_{CF}, proportional to the strain $\Delta a/a$. The result is shown in Fig. 4. As one can see in Figs. 2 and 3, the band gap is slightly indirect, so we display both direct and indirect band-gap values in the figure. We find that for small strain, the band gaps increase linearly as a function of strain, but start to show nonlinear behavior when the strain is large. We find that the band gap is about 58 meV for indirect gap and 73 meV for direct gap when $\Delta a/a \sim 0.03$. This value is smaller than what is found by Gawlik *et al.* for n-type HgSe(001). One possible explanation is that the crystal field at the surface can be larger, and the n-typeness of the sample can cause a Moss-Burnstein shift of the band gap to higher energy values.[28,30]
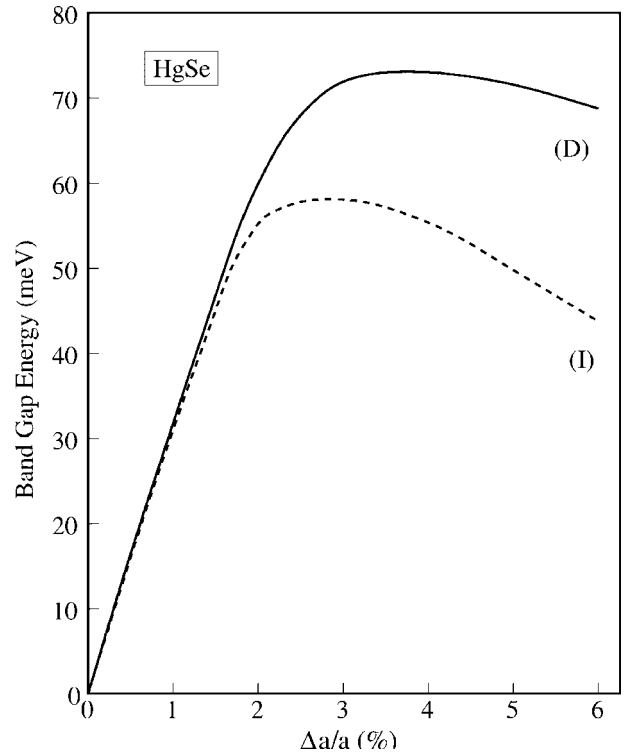

FIG. 4. Band gap of HgSe as a function of biaxial strain $\Delta a/a$. (D) indicates the direct band gap and (I) represents the indirect band gap.

F. Optical absorption

Finally we calculate the momentum matrix element $|\langle\Psi_{\mathbf{k}}^c|\hat{\mathbf{e}}\cdot\mathbf{p}|\Psi_{\mathbf{k}}^v\rangle|^2$ between the highest occupied valence band and the lowest unoccupied conduction band as a function of $\mathbf{k}$ to see whether the optically measured band gap would be consistent with the fundamental band gap. For the ZB structure, we find that the matrix element at Γ point is zero, i.e., the optical transition between the VBM and CBM states at Γ is forbidden. This is expected because for materials with the inverted band structure, both VBM and CBM states at Γ have the same symmetry with mostly anion p character. However, off the Γ point, more and more s orbitals are mixed into the conduction band, hence the matrix elements start to increase. For biaxially strained HgSe with the lowered D_{2d} symmetry, the matrix element at Γ point is still very small, but not exactly zero, because a small amount of s component is incorporated into the states at the Γ point. The matrix elements are nonzero for k points off the Γ point, especially for k points near the VBM and CBM. Therefore, in this case, the optically measured band gap should be similar to the fundamental band gap.

V. SUMMARY

In summary, we find that HgSe and HgTe have inverted band structures (negative band gaps), whereas HgS may have a positive band gap of 0.3 eV. The chemical trend of the band-gap variation can be explained by atomic energy levels and sizes. Using a group theory argument, we show that for

compounds with inverted band structure such as HgSe, an anticrossing band gap could open up when the crystal symmetry is reduced by strain or in the presence of surfaces or interfaces. We find that a relatively large band gap can exist if the material has a relatively large SO coupling and a negative Δ_{CF}. Experimental tests of our predictions are called for.

[1] *Semiconductors: Data Handbook*, 3rd ed., edited by O. Madelung (Springer, Berlin, 2003).

[2] T. L. Tansley and C. P. Foley, J. Appl. Phys. **59**, 3241 (1986).

[3] V. Yu. Davydov, A. A. Klochikhin, V. V. Emtsev, S. V. Ivanov, V. V. Vekshin, F. Bechstedt, J. Furthmuller, H. Harima, A. V. Mudryi, A. Hashimoto, A. Yamamoto, J. Aderhold, J. Graul, and E. E. Haller, Phys. Status Solidi B **229**, R1 (2002); **230**, R4 (2002).

[4] J. Wu, W. Walukiewicz, K. M. Yu, J. W. Ager III, E. E. Haller, Hai Lu, William J. Schaff, Yoshiki Saito, and Yasushi Nanishi, Appl. Phys. Lett. **80**, 3967 (2002); **80**, 4741 (2002).

[5] F. Bechstedt and J. Furthmuller, J. Cryst. Growth **246**, 315 (2002).

[6] S.-H. Wei, X. Nie, I. G. Batyrev, and S. B. Zhang, Phys. Rev. B **67**, 165209 (2003); P. Carrier and S.-H. Wei, J. Appl. Phys. **97**, 033707 (2005).

[7] S. Groves and W. Paul, Phys. Rev. Lett. **11**, 194 (1963).

[8] K.-U. Gawlik, L. Kipp, M. Skibowski, N. Orlowski, and R. Manzke, Phys. Rev. Lett. **78**, 3165 (1997).

[9] A. Mycielski, J. Kossut, M. Dobrowolska, and W. Dobrowolski, J. Phys. C **15**, 3293 (1982).

[10] S. Einfeldt, F. Goschenhofer, C. R. Becker, and G. Landwehr, Phys. Rev. B **51**, 4915 (1995).

[11] M. von Truchsess, A. Pfeuffer-Jeschke, C. R. Becker, G. Landwehr, and E. Batke, Phys. Rev. B **61**, 1666 (2000).

[12] C. Janowitz, N. Orlowski, R. Manzke, and Z. Golacki, J. Alloys Compd. **328**, 84 (2001).

[13] M. Rohlfing and S. G. Louie, Phys. Rev. B **57**, R9392 (1998).

[14] A. Fleszar and W. Hanke, Phys. Rev. B **71**, 045207 (2005).

[15] A. Delin, Phys. Rev. B **65**, 153205 (2002); A. Delin and T. Kluner, *ibid.* **66**, 035117 (2002).

[16] K. J. Siemsen and H. D. Riccius, Phys. Status Solidi **37**, 445 (1970). This paper reported that HgS has an apparent absorption band edge of 0.54 eV, but it also stated that HgS is a semimetal, suggesting that the Γ_6 state is below the Γ_8 state.

[17] P. Carrier and Su-Huai Wei, Phys. Rev. B **70**, 035212 (2004).

[18] S.-H. Wei and A. Zunger, Phys. Rev. B **60**, 5404 (1999).

[19] S.-H. Wei and H. Krakauer, Phys. Rev. Lett. **55**, 1200 (1985); D. J. Singh, *Planewaves, Pseudopotentials, and the LAPW Method* (Kluwer, Norwell, 1994).

[20] P. Blaha, K. Schwarz, and J. Luitz, computer code WIEN2k (Vienna University of Technology, 1997).

[21] N. E. Christensen, Phys. Rev. B **30**, 5753 (1984).

[22] C.-Y. Moon and S.-H. Wei (unpublished).

[23] S. B. Zhang, S.-H. Wei, and A. Zunger, Phys. Rev. B **52**, 13975 (1995).

[24] S.-H. Wei and A. Zunger, Phys. Rev. B **37**, 8958 (1988).

[25] S.-H. Wei and A. Zunger, Appl. Phys. Lett. **72**, 2011 (1998).

[26] N. Orlowski, J. Augustin, Z. Golacki, C. Janowitz, and R. Manzke, Phys. Rev. B **61**, R5058 (2000).

[27] K. Dybko, W. Szuszkiewicz, E. Dynowska, W. Paszkowicz, and B. Witkowska, Physica B **256-258**, 629 (2000). They suggest that the band gap of $Hg_{0.98}M_{0.02}S$ (M=Fe,Mn,Co) is about −0.11 eV. However, in their analysis, they assumed that the band structure of HgS is similar to that of HgSe and HgTe and assumed that the spin-orbit splitting of the valence bands is much larger than the absolute value of the band gap. We find that these assumptions are not valid for HgS.

[28] T. Dietl, W. Dobrowolski, J. Kossut, B. J. Kowalski, W. Szuszkiewicz, Z. Wilamowski, and A. M. Witowski, Phys. Rev. Lett. **81**, 1535 (1998).

[29] M. von Ortenberg, C. Puhle, and S. Hansel, in *Proceedings of 27th International Conference on the Physics of Semiconductors, Flagstaff, 2004*, edited by J. Menendez and C. G. Van de Walle (AIP, Melville, NY, 2005), p. 357.

[30] T. S. Moss, Proc. Phys. Soc. London, Sect. B **67**, 775 (1954); E. Burnstein, Phys. Rev. **93**, 632 (1954).