

First-principles calculations of the II-VI semiconductor β -HgS: Metal or semiconductor

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Relativistic all-electron full-potential first-principles calculations have been performed in order to study the symmetry of the energy levels around the valence band maximum in the zinc blende II-VI semiconductors β -HgS, HgSe, and HgTe. It is demonstrated that in general, an inverted band-structure does not necessarily lead to a zero fundamental energy gap for systems with zinc blende symmetry. Specifically, β -HgS is found to have at the same time an inverted band structure, and a small, slightly indirect, fundamental energy gap. Possibly, the energy levels around the valence band maximum order differently in each of these systems.

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The general question as to whether a material is a metal or not is of basic importance, since the existence of a fundamental energy gap will affect a material's properties in a profound way. Although it appears to be a straightforward matter to detect a fundamental energy gap, several recent examples show that this is not so.

La-doped CaB_6 , ferromagnetic at room temperature and thus a highly interesting material for spintronics, is one example. The ferromagnetism in this system could not be explained until, very recently, *GW* calculations revealed that CaB_6 indeed has quite a substantial fundamental energy gap, contrarily to what was previously thought.¹

Another example comes from the group of materials classified as semimetals. Very few systems are neither real metals, nor semiconductors, nor insulators. This exclusive group is named semimetals and/or zero-gap semiconductors, the most known ones being α -Sn and the zinc blende structured Hg-VI systems β -HgS, HgSe, and HgTe. Whether or not HgSe is a semimetal has recently been subject to controversy,²⁻⁵ and is thus a second example of the ambiguities involved in detecting a fundamental energy gap.

In the present work, it is suggested that β -HgS is actually a semiconductor, and not a semimetal. The approach used is a theoretical one, with calculations based on density functional theory within the local density approximation (LDA). It is well known that fundamental energy gaps are usually underestimated with LDA, but in cases where LDA strongly overestimates hybridization, as in narrow-band *4f* and *5f* systems, LDA may also wrongly produce band gaps not present in reality. The problem then lies in the insufficient description of the correlations, which may be strong in *f* systems. β -HgS is certainly not a strongly correlated system, but nevertheless, there is no guarantee that hybridization is not overestimated in the present calculations. Another point to be kept in mind regarding the present approach is that, since the basis set used in the calculations performed is scalar relativistic, so that all basis functions are zero at the origin, a perfect representation of fully relativistic $p_{1/2}$ states, which are finite at the origin, is in principle precluded. As discussed by Nordström *et al.*,⁶ this becomes important for semicore *6p* states in actinides, for which the spin-orbit coupling is the dominant energy term.

Many of the II-VI systems, including the Hg-VI compounds, alloy with magnetic ions, notably Mn and Fe, to a few tens of percents. These diluted magnetic semiconductors offer unique properties. The interaction of the magnetic ions with the electrons and holes in a narrow band gap semiconductor leads to systems with very large magnetic response, resulting in band gaps tunable in a magnetic field and very large magnetoresistance.⁷ An exciting spintronics application is spin injection into nonmagnetic semiconductors. One example of this is the magnetic II-VI semiconductor $\text{Be}_x\text{Mn}_y\text{Zn}_{1-x-y}\text{Se}$. When used as a spin aligner, injection efficiencies of 90% spin-polarized current into a nonmagnetic semiconductor has been achieved,⁸ which is much higher than what can be obtained with a metallic magnetic material.

Possible spintronics applications are highly relevant in the context of β -HgS, since the calculations presented here demonstrate that the bands around the gap in β -HgS have a highly unusual structure with a negative effective electron mass and unexpected characters. Thus, the electronic structure of β -HgS turns out to be highly unique, and so should also its properties as a spintronics material.

According to the established picture^{9,10} of zinc blende Hg chalcogenides, their electronic structures differ in a fundamental way from the electronic structures of the corresponding isoelectronic Zn and Cd systems in that the Hg systems have "inverted" band structures. More precisely, this means the following. The zinc blende-type Zn and Cd systems are all semiconductors with a positive fundamental energy gap (defined as the difference between the conduction band minimum and the valence band maximum) at the zone center Γ . At the gap, the fully occupied maximum valence band (MVB) has Γ_{15} symmetry (if the spin-orbit coupling is neglected), with place for six electron states, and the empty minimum conduction band (MCB) has Γ_1 symmetry, with place for two electron states. In the Hg systems, the Γ_1 level is pulled down below the Γ_{15} level due to the more attractive potential of the Hg ion compared to Zn and Cd, so that the ordering of the Γ_1 and Γ_{15} levels is inverted. The more attractive potential of the Hg ion is due to a larger partial delocalization of the *d* states in Hg than in Zn or Cd.¹¹ Since the degeneracy of the Γ_{15} level is larger than the degeneracy of the Γ_1 level, the bands connected to the Γ_{15} level are not

all occupied in the Hg systems. Thus, the fundamental energy gap must be zero, and the inverted band structure leads to semimetallic behavior.

If the spin degree of freedom is included, the symmetry of the bands have to be described within the double-group representation. The Γ_{15} level splits into a fourfold degenerate Γ_8 level and a twofold Γ_7 level, with the Γ_8 level above the Γ_7 level for p states, and the Γ_1 level becomes a twofold level of Γ_6 symmetry. If the Γ_6 level is pulled down below the Γ_8 level, or below both the Γ_8 and Γ_7 levels, the MVB and MCB are still degenerate at the zone center, and again the material must have a zero fundamental energy gap.

Therefore, it was very surprising when photoemission experiments² suggested the existence of a positive fundamental energy gap in HgSe, the most studied of the cubic Hg chalcogenides. The observed positive gap was interpreted as evidence for a noninverted band structure. However, more recent photoemission measurements have not been able to reproduce these results, and other experimental methods also obtain a zero fundamental energy gap in HgSe.^{4,9,12} A similar discrepancy exists for β -HgS, whose band gap has been reported to be both “negative” and positive.^{9,13,14}

In the density functional¹⁵ calculations presented here, a full-potential linear muffin-tin method¹⁶ was employed together with the LDA based on the Monte Carlo data calculated by Ceperley and Alder, as parametrized by Perdew and Zunger.¹⁷ Generalized-gradient functionals¹⁸ were also tested, but were seen not to change any of the conclusions put forward here. For Hg, the $6s$, $6p$, and $5d$ orbitals were included in the basis set, and for the chalcogens, the ns , np , and nd orbitals, where $n=3, 4, 5$ for S, Se, and Te, respectively. Two κ^2 values, which determine the form of the basis functions in the interstitial region, were employed in the calculation: -0.8 and -0.1 Ry. The calculations were tested for convergence regarding choice of basis functions, \mathbf{k} -point sampling, and densities of the radial and Fourier meshes. For the calculations with spin-orbit coupling, the entire relativistic Hamiltonian was diagonalized in a single step using the full basis set. The spin-orbit split $6p$ states involved in the present calculation were seen form broad bands, i.e., the spin-orbit coupling was seen not to be the dominant energy term for these states.

In Fig. 1, the LDA bands around the Fermi level, calculated at the experimental equilibrium lattice parameters (5.85 , 6.08 , and 6.46 Å for β -HgS, HgSe, and HgTe, respectively) are plotted from the zone center and out along four different directions (towards L and X in the left column, and towards K and U in the right column). The solid lines represent bands calculated with spin-orbit coupling included, and the dashed lines (left column only) are bands calculated without spin-orbit coupling, but with all other details of the calculation unchanged. When the spin-orbit interaction is neglected, the MVB and MCB are degenerate at the zone center, and form a level of Γ_{15} symmetry. Away from Γ along the Γ - L and Γ - X directions, the Γ_{15} level splits up into a twofold valence band (with place for four electrons), and a onefold conduction band (with place for two electrons).

If the spin-orbit coupling is included, the Γ_{15} splits up into two levels, Γ_8 and Γ_7 . An analysis of the characters of

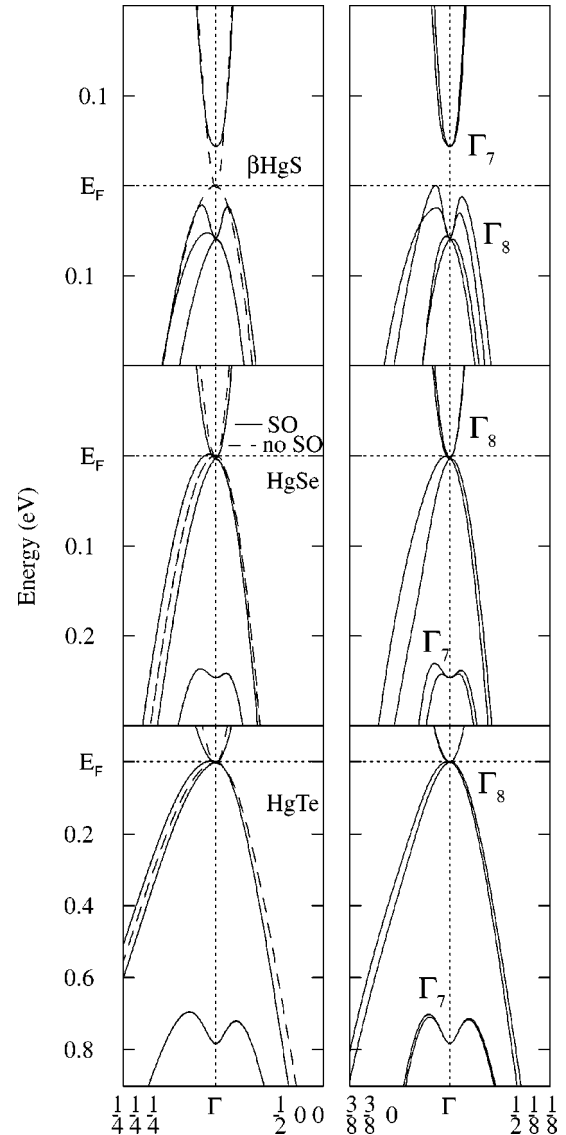


FIG. 1. Band structures around the Fermi level and the zone center Γ for β -HgS, HgSe, and HgTe at the experimental lattice parameters. The Fermi level (or VBM for β -HgS) is at zero. In the left column, the bands are plotted from Γ and half-way to L and X . In the right column, the bands are plotted from Γ and half-way to K and U . The positions in reciprocal space are expressed in units of $2\pi/a$, where a is the lattice parameter. The bands plotted with dashed lines (left column only) are calculated without the spin-orbit (SO) coupling. The bands plotted with solid lines refer to calculations with the spin-orbit coupling included. The representations Γ_7 and Γ_8 refer to the symmetry at the Γ point of the solid bands.

the eigenvalues at the zone center for the bands shown reveals that they lack s character, and that they have Γ_8 and Γ_7 symmetry. In fact, the highest valence band with s character (which is also the next band below the ones shown) is found around 0.7 , 1.2 , and 1.2 eV below the Fermi level for β -HgS, HgSe, and HgTe, respectively. The symmetry of these states is to be Γ_6 , as expected for s states in the zinc blende structure. Thus, the present calculations place the Γ_8 and Γ_7 levels higher than the Γ_6 level in all three systems, although for HgTe, the energy difference between the Γ_6 and Γ_7 levels is

only around 0.4 eV. In HgSe and HgTe, the fourfold Γ_8 level is found above the twofold Γ_7 level, whereas in β -HgS, the ordering is reversed. Because of the difference in degeneracy between the Γ_8 and Γ_7 levels, this reordering opens a fundamental energy gap around Γ in β -HgS. Furthermore, due to the form of the MVB, this gap is slightly indirect. The gap is small, about 0.05 eV in the present calculation but probably around the double in reality, since the discontinuity in the exchange-correlation potential at integer particle numbers in density functional calculations tends to result in underestimated fundamental energy gaps.

What mechanism opens this gap? In the standard tight-binding models for these systems, notably the widely used Kane model,¹⁹ the Γ_8 and Γ_7 levels are implicitly assumed to originate from pure p states. This, however, cannot be correct, since for p states, the Γ_8 level must be higher in energy than the Γ_7 level. This is easily seen by noting that Γ_8 corresponds to $J=3/2$ and Γ_7 to $J=1/2$ for p states, and using $H_{SO}=2\lambda \mathbf{L}\cdot\mathbf{S}=\lambda(J^2-L^2-S^2)$, where H_{SO} is the spin-orbit Hamiltonian, λ the spin-orbit coupling constant, and J , L , and S the usual angular-momentum operators. Note that this explanation implicitly assumes that the Γ_8 states generated from Γ_4 are decoupled from the Γ_8 states generated from Γ_3 , which should be a good approximation in the present case.²⁰

An analysis of the eigenfunctions associated with these levels shows that they have d as well as p character. The energy difference between the Γ_8 and Γ_7 levels is apparently determined by three factors: the chalcogen p spin-orbit splitting, the Hg d spin-orbit splitting, and the strength of the pd hybridization. For p states, the Γ_8 symmetry lies higher in energy than the Γ_7 , whereas the situation is reversed for the d states (Γ_8 corresponds to $J=3/2$ and Γ_7 to $J=5/2$ for d states) so that these two spin-orbit induced band splittings compete. Thus, if the p spin-orbit coupling becomes sufficiently small (like in sulphur), the ordering of the Hg d spin-orbit-split states may decide the order of the Γ_8 and Γ_7 levels. Alternatively, if the d character becomes dominant in these bands due to large pd hybridization, the Γ_7 level might also end up higher than the Γ_8 level. Thus, the Hg d states play a fundamental role in the formation of the gap in β -HgS. Furthermore, one could also say that the fundamental energy gap in β -HgS owns its existence to the *smallness* of the spin-orbit splitting in sulphur (compared to, e.g., selenium), a somewhat counter-intuitive result since with the spin-orbit coupling neglected all together, β -HgS becomes semimetallic.

The zinc blende structured I-VII semiconductors (e.g., CuCl)²¹ have the same ordering of the Γ_8 and Γ_7 levels as proposed here for β -HgS. In that case, however, the d electrons are at the Fermi level, and thus the symmetry properties of d electrons are expected to dominate. Furthermore, since the band structure of the I-VII semiconductors is not inverted, this ordering of the Γ_8 and Γ_7 levels does not give rise to the fundamental energy gap in those systems.

As mentioned, the present calculations place the Γ_6 level well below the Γ_8 and Γ_7 in all three cubic Hg chalcogenides. This is the same ordering as the one found for HgSe in the QP calculations reported by Rohlfling and Louie,³ but

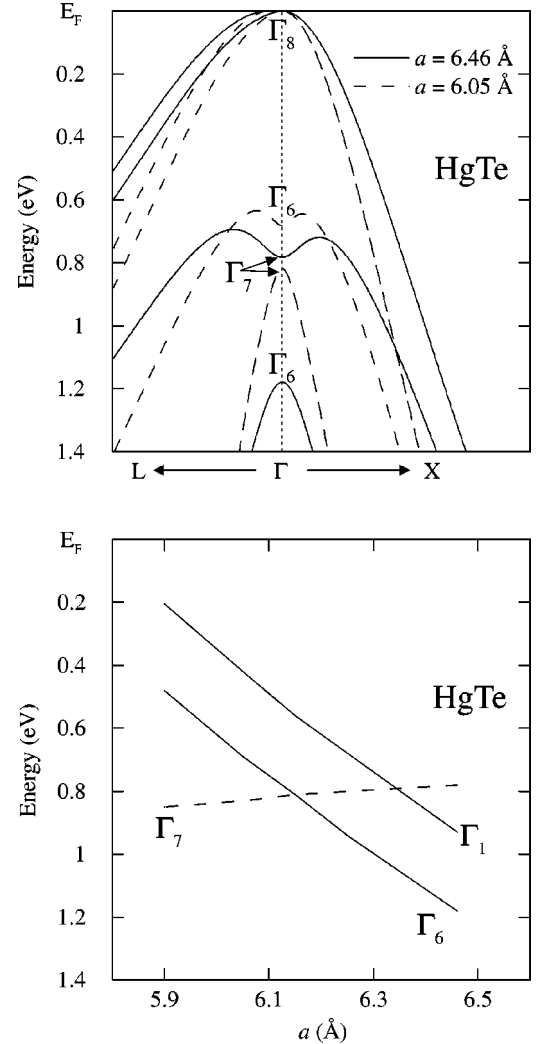


FIG. 2. Upper panel: Band structures for HgTe along parts of the Γ -L and Γ -X directions, showing the bands connected to the Γ_6 and Γ_7 levels at the experimental lattice parameter, and at a compressed lattice parameter. The Fermi level is at zero. At the experimental lattice parameter, the Γ_7 level is above the Γ_6 level, whereas at the compressed lattice parameter, the Γ_6 is above the Γ_7 level. Lower panel: The energy of the Γ_1 , Γ_6 , and Γ_7 levels for HgTe as a function of lattice parameter a .

appears to contradict recent experiments reported by Truchsess *et al.*⁴ for HgSe and Orlowski *et al.*⁵ for HgTe. However, the conclusion regarding the ordering of the highest valence levels in HgSe in Ref. 4 is based on the assumption that electric dipole transitions are symmetry forbidden between the Γ_8 and Γ_7 levels. But, as already demonstrated here, these levels contain both d and p states, and thus, such electric dipole transitions are in fact allowed. With this in mind, the transitions in HgSe observed in Ref. 4 are well explained by the Γ_8 - Γ_7 - Γ_6 ordering predicted by both LDA and QP calculations.

For HgTe, the situation is somewhat different. Here, it might well be that in reality the Γ_6 lies above the Γ_7 level, due to QP corrections absent in LDA calculations. In HgSe, the LDA energy difference between the Γ_6 and Γ_7 levels is more than 1 eV, whereas QP calculations³ predict a much

smaller difference of around 0.2 eV, due to QP corrections for the Γ_6 level. If the QP corrections for the Γ_6 level in HgTe are of the same magnitude, Γ_6 would end up well above Γ_7 .

One way to elucidate, experimentally, the ordering, without having to refer to neither parametrized models nor assumptions regarding the characters of the bands, would be to study how the energy levels move as pressure is applied. The mechanism is illustrated in Fig. 2. In the upper panel, the bands connected to the Γ_6 and Γ_7 levels for HgTe are shown for the experimental equilibrium lattice parameter, and a compressed lattice parameter. Note that at the compressed lattice parameter ($a = 6.05 \text{ \AA}$), the Γ_6 level is above the Γ_7 level. In the lower panel, the positions of the Γ_6 and Γ_7 levels are plotted as a function of lattice parameter. For comparison, also the position of the Γ_1 level is shown, which corresponds to the Γ_6 level when the spin-orbit coupling is neglected.

Apparently, the Γ_6 (or Γ_1) level moves upwards in energy as the pressure is increased. This is in accordance with how the MCB, i.e., the Γ_6 level, behaves in the corresponding Zn and Cd systems.²² In contrast, the Γ_7 level hardly changes at all with pressure, in agreement with the fact that the position of the Γ_7 level is mostly determined by the spin-orbit cou-

pling, i.e., an atomic property. Thus, if the energy difference between the two highest valence bands below the Fermi level decreases with pressure, the ordering is Γ_8 - Γ_7 - Γ_6 , whereas if the opposite pressure behavior is found, the ordering should be Γ_7 - Γ_8 - Γ_6 . The mechanism is illustrated here for HgTe, but is also valid for HgSe.

In conclusion, the calculations presented here suggest that β -HgS has a small, slightly indirect fundamental energy gap. The mechanism opening up the gap in this system is the spin-orbit coupling.

The ordering of the three highest levels at the zone center, Γ_6 , Γ_7 , and Γ_8 is also discussed in detail, and it is argued that the ordering of these levels, and therefore also important parts of the electronic structure, quite plausibly is different in all three Hg-VI compounds.

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