Mercury sulfide HgS is usually found in nature as red cinnabar (α-HgS) which crystallizes in the Se-like trigonal structure which contains angulate Hg–S–Hg chains. Cinnabar constitutes the standard ore for the smelting of elementary mercury. Black HgS, meta-cinnabar, (β-HgS) which crystallizes in the cubic zincblende structure, can be obtained by precipitation in the laboratory as a fine polycrystalline powder which can be easily converted (e.g., by chemical vapor transport) into red cinnabar. Addition of small amounts (≈1%) of Fe helps to crystallize β-HgS in the zincblende structure both in nature, and in the laboratory.

While the electronic and thermal properties of α-HgS appear to be rather well investigated those of β-HgS are less well-known. In this work we describe the vibrational and thermal properties of β-HgS which we carried out by three different approaches [1]: an experimental one and two ab initio electronic structure calculations using different implementations of density functional theory. In order to obtain the electronic structure, we have employed the ABINIT and VASP codes with inclusion of spin-orbit (s-o) interaction. Exchange and correlation effects have been taken care of by the two well-known approximations, LDA (local density approximation) and the PBE-GGA (Perdew, Burke, Ernzerhof generalized gradient approximation).

Additionally, we have obtained the phonon dispersion curves in a quasiharmonic approximation and calculated the heat capacity $C_V$ which we have compared with our new experimental results. The experimental data obtained for natural β-HgS crystals (originating from Mount Diablo Mine, Clayton, CA; 1.1 mass-% Fe according to chemical microanalysis) and on a high purity (99.999%) fine powder sample. Finally, we have also performed calculations of the enthalpy of HgS versus pressure for the zincblende, rocksalt and cinnabar phases. From the dependence on pressure we are able to derive critical pressures at which phase transitions will occur and compared these with experimental results.

**Figure 1:** (a) Electronic band structure of β-HgS calculated with the ABINIT code in the LDA approximation and with s-o interaction using the lattice parameter $a_0 = 5.80\,\text{Å}$ obtained by total energy minimization. (b) Electronic band structure with the energy scale enlarged so as to display the details of the top valence bands, including s-o splitting, and the lowest conduction band around Γ. The $\Gamma_8$–$\Gamma_7$ separation corresponds to the negative s-o splitting $\Delta_0$. $\Gamma_6$–$\Gamma_8$ is the $E_0$ gap. We should mention that Figs. 1(a) and (b) are affected by the so called gap problem which incorrectly lowers the $\Gamma_6$ state with respect to the ($\Gamma_7$–$\Gamma_8$) states. Recent unpublished calculations by Axel Svane suggest that this lowering may be $\approx 1\,\text{eV}$. Thus correcting this effect, as done when using the GW approximation may restore the conventional conduction ($\Gamma_6$)-valence ($\Gamma_8$–$\Gamma_7$) band ordering.
Figure 1 displays the band structure of $\beta$-HgS as calculated with the ABINIT code using the LDA approximation with the energy optimized lattice parameter $a_0 = 5.80 \, \AA$. The wide energy scale chosen in Fig. 1(a) allows us to observe the position of the lowest, sulfur 3s-like $\Gamma_1$ valence band, which is not affected by s-o interaction, at about $-12 \, \text{eV}$. Above this band, the $\Gamma$-s splitting does not split the $\Gamma_1$ states but it splits the $\Gamma_{12}$ sextuplet into a doublet $\Gamma_7$ and a quadruplet $\Gamma_8$, the former being above the latter. The splitting shown in Fig. 1(a) is $2.1 \, \text{eV}$, the same as the corresponding atomic splitting of Hg [2].

At $-0.58 \, \text{eV}$ we find an s-like $\Gamma_1$ state which is composed mainly of 6s states of Hg. This state corresponds to the lowest conduction band for most tetrahedral semiconductors above the $\Gamma_{15}$ valence bands.

In order to resolve the details of the band structure around the $\Gamma$ point we replot in Fig. 1(b) the electronic structure around $\Gamma$ with an expanded energy scale. This figure shows the inverted s-o interaction at $\Gamma$ – the $\Gamma_7$ doublet is above the $\Gamma_8$ quadruplet. This fact arises from the contribution of the negative s-o splitting of the 5d $\Gamma_{15}$ states of Hg which overcompensates the positive splitting of the S 3p contribution. Counting bands we see that the $\Gamma_8$ bands should be occupied whereas the s-o split $\Gamma_7$ should be empty. Hence, according to Fig. 1(b), undoped (intrinsic) $\beta$-HgS should have an indirect energy gap of $\approx 0.15 \, \text{eV}$ and a direct one of $0.18 \, \text{eV}$. This is in reasonable agreement with the gap observed by Zallen and Slade (0.25 eV), although these authors did not realize that the s-o splitting of $\beta$-HgS is negative [3].

A few Inelastic Neutron Scattering (INS) determinations of the phonon dispersion relations of $\beta$-HgS [4], have been published. They have been compared with semiempirical calculations which use fitted force constants. Here we compare the measured points with ab initio calculations and examine the effect of s-o interaction on these calculations. Figure 2(a) displays the phonon dispersion relations of $\beta$-HgS calculated with s-o interaction (solid line) and also without (dashed line). The effect of the s-o interaction (inset for the TA phonons) is rather small, however it is possible to see that for the TA phonons, those mainly responsible for the $C_v$ to be discussed later, the frequencies without s-o are about 5% lower than with s-o.

An interesting feature is the strong upwards bending of the optical bands away from $k=0$, the opposite of what happens for most tetrahedral semiconductors. This effect is due to the large mass difference of Hg and S. At the edge of the zone the ‘effective’ mass which determines the frequency is basically that of sulfur, whereas at $k=0$ it is the somewhat smaller reduced mass. In order to obtain the calculated up-bending one must also invoke a strong force constant connecting the anions.

The upward bending is reflected in the corresponding density of phonon states, shown in Fig. 2(b). A direct consequence is that the TO Raman modes do not overlap the DOS continuum while the LO mode does. The width of the former should therefore not be affected by elastic scattering due to defects, such as isotopic fluctuations, whereas the LO-modes, overlapping the background, should.
The up-bending of the dispersion relations is also important when considering confinement in quantum dots. These effects have been discussed for the case of CdS, a material for which the TO bulk bands bend up but the LO bands bend down [5]. No such experiments are available, to the best of our knowledge, for β-HgS but quantum confinement in dots of this material should produce an increase in frequency as opposed to most other related materials.

Calculations of $C_v$ were performed by integrating the calculated phonon DOS with the standard expression. The calculations were performed both, with the ABINIT-LDA and the VASP-GGA codes, with and without s-o interaction. The effect of s-o interaction was basically the same for the two codes – the s-o interaction lowered the maximum of $C_v/T^3$ by about 10%. We shall present here the results obtained with only one of the codes (except for β-HgS) but both, with and without the s-o interaction. We show in Fig. 3(a) the experimental values of $C_v/T^3$ for two sample of β-HgS, a natural crystal and a high-purity powder. The natural crystal was found by chemical microanalysis to have an Fe content of 1.1 mass-%. The upturn at low temperatures observed for the natural crystal can be ascribed to a linear term in the specific heat (Sommerfeld term) due to metallic behavior. To correct for this term we subtracted a linear contribution $\gamma = 20 \text{ mJ/molK}^2$ from the experimental data. Figure 3(b) displays calculated VASP and ABINIT values of $C_v/T^3$ for β-HgS obtained with and without s-o interaction. The agreement between theoretical and experimental data is reasonably good. Our new measurements seriously question the heat capacity data by Khattak et al. [6] shown for comparison in Fig. 3(a).

Figure 3: (a) $C_p/T^3$ measured on a mineral and a powder sample of β-HgS. Data by Khattak et al. are also given for comparison [6]. The solid line represents the mineral data minus a linear contribution as indicated in the inset. (b) Same mineral data as before compared with the results of four calculations as indicated.

Figure 4: Enthalpy of the three phases of HgS calculated with the ABINIT-LDA code with s-o interaction. Cinnabar and zincblende phases are basically degenerate (within any reasonable error estimates) at $p = 0$ although formally their enthalpies cross at $\approx 0.7 \text{ GPa}$. The cinnabar $\rightarrow$ rock salt transition is predicted to occur at $\approx 22 \text{ GPa}$. Experimental data (not shown) place it at 20.5 GPa [8]. For the sake of clarity the cinnabar enthalpy has been subtracted from all curves.

$C_p$ represents the experimentally measured value of the heat capacity at constant pressure. The ab initio calculations yield $C_v$, i.e., the heat capacity at constant volume. In the temperature region considered here $C_v \approx C_p$. 
Mercury chalcogenides undergo phase transitions at relatively low pressures. While there is considerable experimental data on these transitions [7], no \textit{ab initio} calculations seem to have been reported. We have performed enthalpy minimizations vs. pressure for HgS considering the three most conspicuous structures of these materials: cinnabar, zincblende and rock salt. We show in Fig. 4 the pressure dependence of the enthalpy of the three phases mentioned, as calculated for HgS. The cinnabar phase ($\alpha$-HgS) is found, within estimated error, to have the same enthalpy as the zincblende phase ($\beta$-HgS), a fact which may explain the ease to obtain both phases in the laboratory, although the growth of the zincblende phase requires the addition of a small amount of Fe.

In summary, our \textit{ab initio} calculations of the electronic band structure and the phonon dispersion relations of the zincblende-type $\beta$-HgS predict a negative spin-orbit splitting which restores semiconducting properties to the material in spite of the inverted gap. We have obtained the spin-orbit induced linear terms in $k$ which appear at the $\Gamma_8$ valence bands (not shown here, for details see [1]) and investigated the pressure dependence of the crystal structure and the phonons. The temperature dependence of the specific heat capacity has been calculated and first conclusive low-temperature experimental data on $\beta$-HgS have been presented.

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