Metacinnabar ($\beta$-HgS): a strong 3D topological insulator with highly anisotropic surface states

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We establish the presence of topologically protected edge states on the (001) surface of HgS in the zinc-blende structure using density-functional electronic structure calculations. The Dirac point of the edge state cone is very close to the bulk valence band maximum. The Dirac cone is extremely anisotropic with a very large electron velocity along one diagonal of the surface elementary cell $x'$ and a nearly flat dispersion in the perpendicular direction $y'$. The strong anisotropy originates from a broken fourfold rotoinversion symmetry at the surface.

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Motivated by the ongoing search for spintronics materials, recent theoretical work on the effect of spin-orbit interactions on the band structure of solids predicted the existence of novel topological insulators (TIs) in two [1–3] and three dimensions [4–7]. Topological insulators distinguish themselves from ordinary insulators due to the presence of a non-trivial topological invariant in the bulk band structure [4–8]. Although there is an excitation gap in the bulk as in conventional band insulators, the topological bulk properties dictate that there be gapless modes at the interface between a TI and a topologically trivial state, for instance the vacuum. The surface states of a three-dimensional (3D) TI form massless Dirac cones, with a single Dirac cone being the simplest case. The potential applicability for spintronics arises because the surface states of such a 3D TI appear in time-reversed pairs in which the two electrons have both opposite spin and velocity.

From the material’s viewpoint, two-dimensional (2D) TI behavior was experimentally observed in HgTe quantum wells [9], soon after the theoretical prediction [3]. 3D TIs discovered so far are the binary compounds Bi 170 and Sb 13–17, and the alloy Bi 1−x Sb x 3 14, 15 and very recently, 3D-TI behavior was proposed in certain ternary Heusler compounds [14, 15]. In the former the presence of Dirac cones has been established by photo-emission, but direct electronic transport evidence for metallic surface states on top of an insulating bulk is lacking, mainly because of the small bulk gaps. It is interesting to note that before the advent of TI’s, in semimetallic bismuth surface states were identified that are in hindsight very similar to the chiral surface states of TI’s [16].

Here we establish that metacinnabar, the binary compound $\beta$-HgS, is a strong 3D topological insulator. As opposed to other TI’s discovered to date, the topologically protected Dirac cone on the (001) surface of HgS in the zinc-blende structure is extremely anisotropic. This originates from a broken fourfold rotoinversion symmetry at the surface. The presence of strongly anisotropic topologically protected modes implies highly one-directional spin and electron transport properties providing a natural route to create potentially ideal quantum wires. As this electronic anisotropy is absent in the bulk because it is fourfold rotoinversion invariant, the presence of significant spin and charge transport anisotropy at the (001) surface of HgS will be a smoking gun for its TI nature.

Metacinnabar, $\beta$-HgS, is a gray-black natural mineral, found in mercury deposits that are formed near-surface, under low-temperature conditions. The bulk electronic structure of HgS in the zinc-blende structure has been considered before, with contradicting conclusion on the existence of a band gap inversion [17–19]. Delin [17] and Cardona et al [18] find HgS to be insulating with an unconventional band order at the $\Gamma$ point: the conduction band minimum has $p$-character and the $s$-band, which usually builds the conduction band minimum, is about one eV below the Fermi level. However, according to the electronic structure calculation of Moon and Wei [19], such a band inversion due to spin-orbit interaction is absent. For lattice structures with inversion symmetry the parity criteria of Fu et al [2] guarantee that an inverted semiconductor is a topological insulator, but owing to the lack of inversion symmetry of the zinc-blende crystal structure of $\beta$-HgS these criteria do not apply. We will therefore establish the TI nature of $\beta$-HgS via the bulk-boundary correspondence and explicitly calculate its surface states.

To this end we performed high precision, all electron, full potential and fully relativistic electronic structure calculations for $\beta$-HgS using the FPLO (full potential local orbital) code, version 9.01-35 [20, 21]. We unambiguously establish the presence of an inverted band gap in the bulk material. Investigating in detail the (001) Hg-terminated surface in a slab geometry we demonstrate the presence of a highly anisotropic Dirac cone. This proves that HgS is a topological insulator. The anisotropy of the cone implies that the velocity and mo-
bility of the charge carriers at the surface is very high in one direction and low in the direction perpendicular to it. Thus it will strongly affect surface spin and charge transport.

To calculate the bulk band structure of the zinc-blende crystal we used the experimental lattice parameter \( a_0 = 5.85 \text{ Å} \), incidentally equal to the theoretical value (Fig. 1). Without spin-orbit (SO) coupling, all three 3p-orbitals of S would be degenerate leading to metallic behavior. The SO-coupling splits the 3p-orbitals into a lower quartet (3p\(_{3/2}\)) and an upper doublet (3p\(_{1/2}\)) with a gap of 109 meV at the Γ-point. The indirect gap between conduction and valence band is 42 meV. The band of s-character (here Hg 6s) which builds the conduction band minimum in ordinary semiconductors is found at 0.65 eV below the Fermi level. This level inversion, in connection with the electron-like dispersion of the valence band at the Γ-point, implies that HgS is an inverted semiconductor, which is a prerequisite for it to be a topological insulator.

The insulating character of HgS is related to the fact that the sulfur quartet (3p\(_{3/2}\)) is below the doublet (3p\(_{1/2}\)) which contradicts the third Hund’s rule for pure p-orbitals. The related compounds HgSe and HgTe, in which the Hg 6s level is far below the Fermi level too, have the “correct order” with the doublet below the quartet. Accordingly, there is no gap in those two compounds. The reversed SO-order in HgS (quartet below doublet) comes about because of a small but significant contribution of Hg 5d orbitals whose SO-coupling dominates the one of S 3p and reverses the sign. So, contrary to naive expectations it is actually the smallness of the SO-coupling parameter of the sulfur p orbitals (in contrast to the p orbitals of Se or Te) \([17]\) which allows HgS to become a topological insulator.

Since HgS has an inverted level order at the Γ-point, its topological invariant can be non-trivial and thus be different from the vacuum. This implies a change of topology at any surface and hence the presence of gapless surface states. An explicit calculation of the topological invariant of HgS is technically more involved as the simple definition for lattices with inversion symmetry cannot be applied for zinc-blende crystals which lack this symmetry \([22]\). Therefore, we studied in detail the (001) surface of β-HgS and calculated its electronic structure explicitly, establishing the topological structure of the bulk via the bulk-boundary correspondence \([7, 8]\). To this purpose we performed electronic structure calculations of HgS slabs, varying the thickness. To guarantee electro-neutrality of the surface each second Hg-atom has to be removed from a Hg-terminated surface (see Fig. 2). The surplus Hg-atoms in the top and bottom layers were removed in a checker-board pattern, so that the slab has tetragonal symmetry. Such a surface reconstruction is known from similar surfaces like for instance the (100) surface of WO\(_3\) \([23]\). We have also considered S-terminated surfaces but they are less relevant to the present discussion as we find such a termination to be 265 meV per surface elementary cell higher in energy and therefore substantially less stable.

The HgS slab that we consider has a tetragonal supercell (space group 111) consisting of (001) stacks of conventional cubic elementary cells, spaced by an empty (vacuum) layer of 23.4 Å thickness. The experimental cubic lattice parameter, \( a_0 = 5.85 \text{ Å} \), was used as in the bulk calculations. Self-consistent calculations were performed in a scalar-relativistic mode, using the local density approximation in the parameterization of Ref. \([24]\). The presented band structures were evaluated in the fully relativistic mode (four-component Dirac-Kohn-Sham scheme) using a dense \( k \)-point mesh of \( 25 \times 25 \times 1 \) intervals in the full Brillouin zone and linear tetrahedron integration with Blöchl corrections in order to ensure the correct position of the Fermi level. The valence basis set comprised sulfur (2s, 2p, 3s, 3p, 3d, 4s, 4p) and mercury (5s, 5p, 5d, 6s, 6p, 6d, 7s) states.

We systematically studied slabs containing \( n \) elemen-
The two resulting Dirac cones are almost degenerate in the direction \( \Gamma - X \) but in the direction \( \Gamma - M \) they split up because of the broken fourfold rotoinversion symmetry at the surface. The direction \( \Gamma - M \) corresponds to the diagonal \( k_x' = (k_x + k_y)/\sqrt{2} \) which is identical to the other diagonal \( k_y' = (k_x - k_y)/\sqrt{2} \) in the tetragonal, rotoinversion symmetric electronic structure of the slab (space group 111), but not at either of the surfaces. In fact, the Dirac cone with the large dispersion along \( k_x' \) belongs to the top surface and the other one with two nearly flat bands above and below the crossing point corresponds to the bottom surface. Along the other diagonal, these roles are interchanged. Indeed, considering just the top Hg-layer and the sulfur atoms in the sub-surface layer, one observes a chain-like structure along one of the diagonals (see Fig. 2). As will become more clear from the continuum model below, the anisotropy can effectively be described by a crystal field splitting of \( p \)-orbitals that build the Dirac cone of the surface.

To illustrate our band structure results we construct a simple two-dimensional (2D) model that describes the anisotropic "Dirac cone". This model displays essential features of the slab band structure in the neighborhood of the \( \Gamma \)-point. It uses two perpendicular \( p \)-like orbitals with different on-site energies \( \epsilon_x' \) and \( \epsilon_y' \) (crystal field splitting) and directed along the two diagonals of the elementary cell \( x' = (x + y)/\sqrt{2} \) and \( y' = (x - y)/\sqrt{2} \). The crystal field splitting accounts for the fact that the fourfold rotoinversion symmetry is broken at the surface. The two \( p \)-like orbitals will be denoted as \( |p_x,s\rangle \) (for the two spin directions \( s = \uparrow \) or \( \downarrow \)) and \( |p_y,s\rangle \). The \( p \)-like orbitals are no eigenstates of the local SO-coupling operator \( \lambda \mathbf{s} \) but the corresponding coupling elements are easily calculated. The SO-coupling gives also rise to spin-flip hopping in both directions \( \alpha_k \sigma_x \sigma_2 \) and \( \alpha k_y \sigma_1 \). Finally, there are the known tight-binding hopping elements corresponding to \( \sigma \)-bonds (strength \( A \)) and \( \pi \)-bonds (strength \( B \)). In the continuum limit this Hamiltonian is cast in the form of the 4 by 4 matrix

\[
H = \begin{pmatrix}
E_{x'} \sigma_0 + \alpha k_y \sigma_2 & -i(\lambda/2) \sigma_3 \\
\alpha k_x \sigma_3 & E_{y'} \sigma_0 + \alpha k_y \sigma_1
\end{pmatrix}, \tag{1}
\]

where \( \sigma_0 \) and \( \sigma_{1,2,3} \) are the identity and three Pauli matrices, respectively, and \( E_{x'} = \epsilon_x' + A k_x^2 + B k_y^2 \) and \( E_{y'} = \epsilon_y' + A k_y^2 + B k_x^2 \).

All momenta \( k_x \) and \( k_y \) are expressed in units of \( 1/a_0 \) with \( a_0 = 5.85 \) Å. The two upper bands of that model fit the band structure of the 8-layer slab in the neighborhood of the \( \Gamma \)-point with the following parameters (see Fig. 3): \( \lambda = -0.05, \alpha = 0.25, \Delta E = \epsilon_x' - \epsilon_y' = 0.1, A = 0.8, \) and \( B = -0.1 \) (all values in eV). For the two relevant surface bands, in the neighborhood of the \( \Gamma \)-point, the model [1] can be further reduced to the anisotropic, massless Dirac Hamiltonian

\[ H = \alpha_{x'} k_x \sigma_1 + \alpha_{y'} k_y \sigma_2, \]

with \( \alpha_{x'} = \alpha \cos^2 \gamma, \alpha_{y'} = \alpha \sin^2 \gamma \).
very sensitive to the surface anisotropy of the electronic structure that is absent in bulk.

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