Predicted topological phase transition in the SmS Kondo insulator under pressure

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Employing density functional calculations we predict that SmS undergoes a topological phase transition from the trivial Kondo insulator (KI) black phase to a topological metallic gold phase under hydrostatic pressure. The underlying mechanism is the pressure-induced change of the $4f$ level from below to above the bottom of the $5d$ conduction band, leading to a $d$-$f$ band inversion, a parity sign reversal, and the concomitant change of the topological invariant $\nu$. This provides a material realization of the topological classification of KIs proposed by Dzero et al.

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Three-dimensional (3D) topological insulators (TIs), distinguished from ordinary insulators by the $Z_2$ topological invariant \cite{1-4}, are new states of quantum matter which are fully gapped in the bulk of the material but have gapless Dirac fermion states on the surface protected by time-reversal symmetry. Due to the strong spin-orbit coupling (SOC) in these materials, the surface states display an unconventional spin helical texture with the spin direction locked to the two-dimensional electron momentum. Ongoing research efforts focus primarily on the prototypical family of weakly correlated 3D TIs, Bi$_2$Te$_3$, Bi$_2$Se$_3$, and Sb$_2$Te$_3$, where an effective single-electron picture for the electronic structure provides an adequate description.

More recently, the search for novel topological insulator states has extended to the family of correlated TIs, where the interplay between strong electron-electron interactions and the SOC gives rise to topological Mott insulators \cite{5} and topological Kondo insulators (KIs) \cite{6,7}. Dzero et al. \cite{6,7} employing the periodic Anderson lattice model developed a topological classification of the emergent bands for KIs, where the topologically nontrivial insulating state depends on the position of re-normalized $f$ level relative to the bottom of the conduction band and the momentum-dependent conduction-$f$ electron hybridization due to the strong SOC interaction on the $f$ sites. The conditions for strong TIs are more likely fulfilled in the mixed valent limit of the Kondo problem, such as in the SmB$_6$, YbB$_{12}$, and CeNiSn compounds, containing rare-earth elements with noninteger chemical valence. Subsequent density functional theory (DFT) calculations \cite{8} employing the local density approximation (LDA) + Gutzwiller method predicted that SmB$_6$ is a strongly correlated TI whose surface states contain three Dirac cones. Recent frequency coding limit cycle and anomalous capacitance \cite{9} experiments and surface conductivity \cite{10,11} measurements have suggested that SmB$_6$ is a TKI. More recently, density functional theory calculations based on the local density approximation (LDA) and the dynamical mean field theory (DMFT) predicted that the simple cubic PuB$_6$ \cite{12} is a strongly correlated topological insulator.

Among the strongly correlated KIs, SmS has attracted great interest \cite{13-20} during the past several decades due to its valence and semiconductor-to-metal transition (“black-gold” phase transition) at a relatively low pressure, $p_{B-G} \sim 0.65$ GPa, at room temperature. At ambient pressure SmS is a nonmagnetic semiconductor (black phase) with a small band gap of $\sim 0.15$ eV where the Sm ions have a divalent configuration ($4f^6$) \cite{21,22}. At $p_{B-G} \sim 0.65$ GPa and room temperature it undergoes an isostructural (NaCl-type) first-order phase transition to a metallic phase (gold phase) with a large volume collapse of $\sim 8\%$ \cite{17,22}. Gold SmS is a homogenous mixed valence state with a Sm valence ranging from 2.6 to 2.8. In the black phase the $4f$ levels, $E_{4f}$, lie between the valence and $5d$ conduction band split by the crystal field into $t_{2g}$ and $e_{g}$ subbands. Upon increasing the pressure the bandwidth of both the $4f$ and $5d$ states increases and at $p_{B-G}$ the $5d$ band overlaps with the $4f$ levels giving rise to a charge transfer from the $4f$ state to the $5d$ conduction band and a concomitant intermediate mixed valence state.

Because of the fluctuating valence and charge transfer between $4f$ and $5d$ orbitals under high pressure \cite{23}, the SmS KI offers a unique playground for realizing the trivial-to-nontrivial transition proposed by the tight-binding model calculations of Dzero et al. \cite{6}. Furthermore, recent LDA + $U$ calculations for the Pu chalcogenides, which are the actinide counterpart of the Sm chalcogenides (the electronic configuration of the Pu and Sm atoms is $5f^6d^0s^2$ and $4f^6d^0s^2$, respectively), have predicted that they are strong TIs at ambient pressure \cite{5}. The rocksalt-structure Pu chalcogenides do not show magnetic order, have anomalous lattice constants, which are too small for both divalent ($5f^6$) and trivalent ($5f^3$) Pu ions, and their room-temperature band gap increases under pressure contrary to conventional knowledge. In contrast, the $4f$ shell in the Sm chalcogenides has smaller radial extension compared to that of the $5f$ shell giving rise to larger $4f$-$4f$ intra-atomic electron interaction, weaker $4f$-$5d$ hybridization which vanishes somewhere in the zone, and narrower $4f$ bands.

In this Rapid Communication, we employ density functional calculations based on the LDA and the modified Becke-Johnson LDA \cite{24} plus Hubbard $U$ (MBJLDA + $U$) approach to investigate the effects of $4f$ correlation and pressure on the topological nature of SmS. The MBJLDA + $U$ calculations predict that the black phase of SmS is a trivial insulator and undergoes a transition to a nontrivial topological metallic state in the gold phase. This is a material realization of the...
topological classification of KIs proposed by Dzero et al. [6]. We demonstrate the topological nature by calculating the $Z_2$ topological invariant which characterizes the global band topology of the occupied Bloch wave functions in the entire Brillouin zone (BZ). This result is further corroborated by the product of the parities for all the occupied states at the time-reversal-invariant momenta (TRIM) points. At ambient pressure inclusion of the intra-atomic Coulomb interaction suppresses the charge transfer between the $4f$ and $5d$ orbitals and renders the band topology of SmS trivial. The underlying strength of the re-normalized $f$ orbitals suppresses the charge transfer between the $4f$ and $5d$ orbitals. This result is further corroborated by the evolution of the band structure and the concomitant $4f$-$5d$ band inversion at the X TRIM points.

The ab initio electronic structure calculations employed the all-electron, full-potential linearized augmented plane wave (FPLAPW) method implemented in the WIEN2K code [25]. To better account for the on-site $4f$-electron correlations, we apply the MBJLDA [24] plus $U$ approach that incorporates an on-site Coulomb repulsion $U$ and Hund’s rule coupling strength $J_H$ with an approximate correction for self-interaction correction (SIC) [26] for the Sm $4f$ states. We used $R_{MT} \times K_{max} = 9.0$, muffin-tin radii of 2.50 a.u. for Sm and 2.30 a.u. for S, respectively, and a $25 \times 25 \times 25$-k-point Monkhorst-Pack mesh. We have used the experimental values of 5.97 Å and 5.60 Å for the black and gold phases, respectively. The spin-orbit coupling was included in the self-consistent calculations and the on-site Hund’s exchange parameter $J_H$ was set to zero. The basis set consisted of the Sm $4f$, $5d$, $6s$, and $6p$ valence states, the Sm $5s$ and $5p$ states semicore states (treated in a different another energy window), and the S $3s$ semicore and $3p$ valence states.

The calculated value of $U$ can depend on theoretical approximations and it may be better to regard the value of $U$ as a parameter and try to specify it from comparison of the calculated physical properties with experiments. The $Z_2$ is determined by the evolution of the Wannier function center (WFC) in reciprocal space during a “time-reversal pumping” process [27–31]. This corresponds to the phase factor $\theta$ of the eigenvalues of the position operator $\hat{X}$ projected into the occupied subspace. $Z_2$ is then calculated by the even or odd number of crossings of the evolution of $\theta$ with an arbitrary horizontal $(\theta = \text{const.})$ reference line, mod 2. For a 3D TI, it is necessary to calculate the invariants, $(Z_2)_0$ and $(Z_2)_\pi$, for the two different BZ planes, $k_z = 0$ and $k_z = \pi$. The system is a TI (trivial insulator) if the “strong” topological invariant, $\nu_0 \equiv [(Z_2)_\pi - (Z_2)_0]$ (mod 2) is 1 (0). Since SmS has crystal inversion symmetry we have also calculated $Z_2$ as the product of half of the parity (Kramers pairs have identical parities) numbers, $\delta_i$, for all the occupied states at the TRIM points [32], $(−1)^\nu = \prod_{i=1}^{8} \delta_i$.

Black phase. Figure 1 shows the band structure of SmS calculated with the LDA at the experimental lattice constant of 5.97 Å for the black phase. The calculation reveals that SmS is semimetallic with positive direct energy band, but negative indirect band gap, which is not consistent with the experimental results that SmS is a semiconductor with a low band gap of ~0.15 eV [22]. Each band is twofold degenerate, and the correlated $f$ bands split into occupied $f_{5/2}$-derived bands and unoccupied $f_{7/2}$-derived bands due to the large SOC (~1.0 eV). The $f$-derived bands are flat and pinned at the Fermi energy along the W-L direction, but become dispersive along the $\Gamma$-X direction, similarly to the band dispersion of the $5f$ states in PuTe [5]. The dispersive electronic bands above the Fermi energy ($E_F$) are derived mostly from Sm 5d states. The bands of primarily $4f$ character are thus placed energetically in between the $3p$ bands, which are about 4 eV (not shown in Fig. 1) below $E_F$, and the Sm 5d bands. The samarium $4f$ bands hybridize with the $5d$ bands throughout the BZ, except at the TRIM points where the $f$-$d$ hybridization vanishes identically, because of the opposite parity of the Sm $4f$- and $5d$-derived states. The weight of the orbital character for the $4f$ and $5d$ states is denoted by blue and red, respectively. Interestingly, the $d$ orbital and $f$ orbital are hybridized into the $\Gamma_7^+$ band around the X point.

In analogy with the topological semimetal AuTlTe [33], the topological characterization of the valence energy bands of the semimetallic SmS is still possible due the finite direct band gap throughout the BZ [32]. The band structure of SmS has a nontrivial topology because of the band inversion between the $4f$-derived and $5d$-derived states at the X point $[\pi(110)]$. Since the $d$ orbitals are even (odd) under spatial inversion, the product of parities (Table I) of the occupied bands at the three X TRIM points is positive, while that for the other two TRIM points ($\Gamma$ and four L TRIM points) is negative, similarly.
TABLE I. The product of parity eigenvalues for all occupied states at the $\Gamma$, three $X$, and four $L$ TRIM points in the BZ, and the total parity product of all TRIM points, employing the LDA and the MBJLDA + $U$ approaches, respectively. The $+$ and $-$ denote even and odd parity, respectively.

<table>
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<th>$\Gamma$</th>
<th>3X</th>
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<tr>
<td>LDA (black phase)</td>
<td>$-$</td>
<td>$+$</td>
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<tr>
<td>MBJLDA + $U$ (black phase)</td>
<td>$-$</td>
<td>$-$</td>
<td>$-$</td>
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<tr>
<td>MBJLDA + $U$ (gold phase)</td>
<td>$+$</td>
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to the case of PuTe. Thus, the LDA method renders SmS a topological semimetal.

We have also carried out calculations employing the MBJLDA [24], which yields accurate band gaps, effective masses, and frontier-band ordering, which are crucial for the correct determination of the TI phase [34]. While the MBJLDA describes accurately the correlation effects of the 5$d$ states, it cannot capture well those of the more localized 4$f$ states, whose treatment still requires a small $U$ value [35,36]. This is similar to the $GW + U$ approach [37], which was also put forward to fix the $GW$ problems for 4$f$ systems. The MBJLDA + $U$ calculations with $U$ of $\sim 3.0$ eV yields a band gap $\sim 0.20$ eV, which is in good agreement with experiment. In Fig. 2(a) we show the band structure of SmS calculated with the MBJLDA + $U$ method at the experimental lattice constant of 5.97 Å for the black phase, in agreement with the fully relativistic Dirac LMTO band structure calculations [15].

As shown schematically in Figs. 3(a) and 3(b) the intraatomic Coulomb interaction shifts downward the energies of the lower Hubbard band (LHB), which consists of mixed 4$f_{5/2}$ and 4$f_{7/2}$ states, and narrows its bandwidth. The LHB becomes fully occupied and lies in the gap between the the $S\ 3p$ states and the Sm 5$d$ states. On the other hand, it shifts upward the upper Hubbard band (UHB) which also consists of mixed 4$f_{5/2}$ and 4$f_{7/2}$ states. The UHB is completely unoccupied and hybridizes with the Sm 5$d$-derived states. This results in a complete suppression of electron charge transfer between the Sm 4$f$ and 5$d$ states and hence a divalent Sm$^{2+}$ configuration at ambient pressure. The weight of the orbital character for the 4$f$ and 5$d$ states is denoted by blue and red, respectively. The shift of the 4$f$ band below the 5$d$ band near the X TRIM point leads to a band inversion and hence a parity sign reversal at X (from positive to negative), as listed in Table I, rendering SmS a topological trivial band insulator, consistent with the prediction of Dzero et al [6].

Gold phase: Effect of pressure on topological transition. The topological classification of the band structures for KIs [6] invites an intriguing question: Could the pressure-induced change of the 4$f$ level from below to above the bottom of the 5$d$ conduction band lead to a transition from a trivial topological insulator at ambient pressure to a topological metallic state? As shown schematically in Figs. 3(b) and 3(c), the pressure increases the bandwidth of the 5$d$-derived states and induces a charge transfer between the 4$f$ and 5$d$ orbitals changing in turn SmS in a mixed-valence phase.

Figure 2(b) displays the band structure of SmS calculated with the MBJLDA + $U$ method at the experimental lattice constant of 5.60 Å for the gold phase, where $U = 3.0$ eV. Comparing Figs. 2(a) and 2(b), it is seen that the fully occupied LHB below $E_F$ in Fig. 2(a) shifts upward and becomes partially occupied while the 5$d$-derived bands shift downward, and the phase semimetallic, as expected. This leads to a $d$-$f$ band inversion at the X TRIM point, where as shown in Table I the parity changes from "odd" at ambient pressure to "even" at $p_{B-G} \sim 0.65$ GPa, inducing a transition from a trivial topological insulator state to a topological metallic state. Furthermore, as the volume is reduced the 5$d$ and 4$f$ bands become increasingly hybridized, and the $d$ and $f$ bands become broader [also shown schematically in Fig. 3(c)]. The hybridized 4$f$ and 5$d$ bands near the X TRIM point can be described by an effective low-energy Hamiltonian [6,38] which has two hybridized bands of the form

$$E_{\pm} = \frac{1}{2} \left[ \langle \xi_d(k) \rangle + \epsilon_f(k) \pm \sqrt{\langle \xi_d(k) \rangle^2 - \epsilon_f(k)^2 + 4 |V_{df}(k)|^2} \right],$$

where $\langle \xi_d(k) \rangle$ is the bare band dispersion of conduction (localized) 5$d$ (4$f$) orbital, and $V_{df}(k)$ is the momentum-dependent hybridization between 5$d$ and 4$f$.
In order to corroborate the $d$-$f$ band inversion and the concomitant sign reversal of the parity at the XTRIM point we have also calculated the $Z_2$ topological invariant employing the MBJLDA + $U$ method at the experimental lattice constants for the black and gold phases. The evolution curves of the Wannier [29,39,40] centers along the $k_y$ direction in the $k_z = 0$ and $k_z = \pi$ planes are shown in Figs. 4(a) [4(c)] and 4(b) [4(d)] for the black (gold) phase, respectively. For the black phase the evolution curves cross any arbitrary line parallel to the horizontal axis an even number of points for both the $k_z = 0$ and $k_z = \pi$ planes, thus yielding $\langle Z_2 \rangle_0 = \langle Z_2 \rangle_\pi = 0$ and $\nu_0 = 0$, confirming that the phase is indeed a trivial topological insulator. In sharp contrast, for the gold phase the evolution curves cross any arbitrary line parallel to the horizontal axis an even (odd) number of points for the $k_z = 0$ ($k_z = \pi$) plane, thus yielding $\langle Z_2 \rangle_0 = 0$, $\langle Z_2 \rangle_\pi = 1$, and $\nu_0 = 1$, confirming its topological metallic nature.

In summary, we predict that SmS undergoes a topological phase transition from the trivial Kondo insulator black phase to the topological metallic gold phase under hydrostatic pressure. The underlying mechanism is the pressure-induced change of the $4f$ level from below to above the bottom of the 5$d$-derived conduction band due to the increase of the 5$d$ bandwidth with decreasing lattice constant. Consequently, the charge transfer between the 4$f$ and 5$d$ orbitals leads to a $d$-$f$ band inversion and a parity sign reversal at the X TRIM point, and the concomitant change of the topological invariant $\nu_0$. This provides a material realization of the topological classification of KIs proposed by Dzero et al. [6]. The calculations also demonstrate that inclusion of the intra-atomic correlation effects at ambient pressure change the topological nature of the black phase from topological metallic to a topological trivial insulator state.

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[34] Yoon-Suk Kim, Martijn Marsman, Georg Kresse, Fabien Tran, and Peter Blaha, Phys. Rev. B 82, 205212 (2010).