Topological Phase Transition in Sb$_2$Mg$_3$ Assisted by Strain

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Supporting Information

ABSTRACT: Topological insulating materials with dissipationless surface states promise potential applications in spintronic materials. Through density functional theory, we proposed a new class of topological phase transition in Sb$_2$Mg$_3$ on the basis of tensile strain. At the equilibrium state, Sb$_2$Mg$_3$ corresponds to a normal insulator, and under the influence of tensile strain, the band gaps are gradually tuned. At $\varepsilon = 7.2\%$, the nontrivial phase is achieved due to spin–orbital coupling (SOC), and a nontrivial topological phase band gap of 0.22 eV is opened. As a result, the Dirac cone is locked in the bulk, which is associated to $P_{xy}$ band crossing. Interestingly, the tuning of nontrivial topological properties with tensile strain leading to spin saturation indicates an orbital-filtering effect. The surface state of the Sb$_2$Mg$_3$ material is determined by the topological invariant, $Z_2 = 1$, at the critical tensile strain in the presence of the SOC effect. This study enhances the scope of topological insulators and current platforms to design new spintronic devices.

1. INTRODUCTION

The emergence of topological insulators (TIs) initiated a new concept to pursue nontrivial topological phases in quantum materials, especially in the band theory of quantum solids. The novel applications have motivated the search for new materials exhibiting topological properties, for which new theoretical insights are required. Subsequently, several techniques such as doping or changing of the composition, pressure, strain, and electric field have been used to control topological phase transition in materials.

Topological systems promise interesting applications, such as better catalysts or new magnetic storage media and more energy-efficient microelectronic components. Several attractive new classes of topological materials have been discovered, including topological crystalline insulators (TCIs) and topological insulators (TIs), and were achieved by SOC-induced parity inversion of the valence band (VB) and conduction band (CB) as a guiding principle. Contrarily, Dirac semimetals (DSMs) touch the Fermi level in the band structure calculation. The bulk band gap of nontrivial topology can be closed, and therefore, the energy level of the topologically protected metallic bulk states is critical in a topological quantum phase transition (TQPT). This has been enhanced by tuning an intrinsic material property such as SOC interaction by chemical doping or alloying of the composition. For instance, a phase change from the nontrivial phase to the trivial phase has been carried out in TIBiSe$_2$–S$_x$ and Hg$_{1-x}$Cd$_x$Te. Such a nontrivial phase can also be obtained using an external pressure without the explicit requirement of alloying or doping. This approach avoids the problem of unwanted inhomogeneity and defects typically arising due to alloying. Therefore, it has become an attractive method for examining quantum phase changes in TIs. Recently, topological phase transitions have been observed in several materials by applying tensile strain modification. Pressure leading to nontrivial phase transition has been reported in polar semiconductors BiTeBr and BiTeI, rocksalt chalcogenides, Pb$_{1-x}$Sn$_x$, and layered materials.

For experimental observation of the topological phase transition through detection of the gapless metallic surface states, angle-resolved photoemission spectroscopy (ARPES) and scanning tunneling microscopy are utilized. Unfortunately, observing the surface state at high pressure using ARCES is difficult, thereby making it experimentally challenging to investigate hydrostatic pressure or quantum phase transitions in TIs that can be obtained by applying strain. Furthermore, first-principles studies add an achievable alternative to explore the existence of such phase transitions and also to characterize unique surface states through simulations. Therefore, there has been renewed interest in theoretically probing strain-induced topological phase transitions in topological materials.

In this article, based on density functional theory calculations, we report topological phase changes in Sb$_2$Mg$_3$. This material is a normal insulator at the equilibrium state, and its band gap decreases under induced tensile strain. Hence, the material transforms into a Dirac semimetal without SOC at applied $\varepsilon = 7.2\%$. In the presence of SOC, the band gap reopens under the influence of time reversal-invariant momenta.

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Figure 1. (a) Bulk crystal structure of Sb$_2$Mg$_3$. (b) Bulk and projected surface Brillouin zones. The four TRI points are Γ (0, 0, 0), L (π, 0, 0), F (π, π, 0), and Z (π, π, π). The hexagon indicates the 2D Brillouin zone of the projected (1, 1, 1) surface in which the high-symmetry k points Γ, K, and M are labeled. (c) Phonon dispersion along the bulk Brillouin zone.

2. RESULTS AND DISCUSSION

An alkali-metal antimonide class of compounds has gained attention due to its potential exotic physical properties. Sb$_2$Mg$_3$ crystallizes both in hexagonal and cubic bixbyite structures. The α-phase is the high-temperature phase with 80 atoms in the unit cell (32 Sb and 48 Mg) prototypical of La$_2$O$_3$. Under ~1200 K, with the unit cell consisting of five atoms (two Sb and three Mg), the α-phase transitions to a β-phase structure.

The optimized lattice parameter for the hexagonal phase of Sb$_2$Mg$_3$ is $a = b = 4.61$ Å and $c = 7.27$ Å, as illustrated in Figure 1a, with two Sb and three Mg atoms in the unit cell. The cohesive energy of Sb$_2$Mg$_3$ described as the difference between the energy of the free three Mg and two Sb atoms and the total energy of Sb$_2$Mg$_3$ in the solid phase is calculated to be $-0.752$ eV. Furthermore, the stability of this crystal is confirmed by phonon dispersion along the bulk Brillouin zone (Figure 1b), in which the nonappearance of the imaginary frequency indicates that the material is dynamically stable, as presented in Figure 1c. Since the primitive cell contains five atoms, a factor group analysis leads to 15 vibrational modes at the Γ point, of which 12 are optical modes and 3 are acoustic modes.

Moreover, we performed ab initio molecular dynamics (MD) simulations at 300 and 500 K with a $4 \times 4 \times 4$ supercell under periodic boundary conditions for 10 ps with a time step of 1.0 fs. The temperature versus time graph remains the same for variations between 290 and 310 K at 300 K.

The same observations have been found between 490 and 510 K at 500 K, as presented in Figure S1a,b. The results show thermal stability for Sb$_2$Mg$_3$.

As plotted in Figure 2a, an indirect band gap of 0.43 eV is observed, where the VBM is located at the Γ point and the CBM is found between Z and F of the bulk Brillouin zone. The valley degeneracy is 2 for the CBM at the Z–F point, and the high valley degeneracy is 6 for the accurate CBM at the CB point along the Z–Γ line. Thus, n-type Sb$_2$Mg$_3$-based Zintl compounds are confirmed to be high-performance thermoelectric materials with multiple degenerate valleys and low lattice thermal conductivities. Spin–orbital coupling has no influence on the CB; however, only a small reduction in the band gap and in the VB was observed, as illustrated in Figure S2a,b.

The hybrid HSE06 functional is adopted to check the accuracy of the band gap calculation, considering that the PBE functional generally underestimates the band gap, as presented in Figure 2a,b, and the energy gap is calculated to be 0.46 eV. It is particularly interesting that, for the band structure without the inclusion of SOC, the VBM is mainly determined by the Sb-p$_x$ orbitals related to the bands with Sb-p$_x$, whereas the CB has a (Mg)Sb-s orbital character with little influence on the band structure by Sb-p$_y$, as shown in Figure S3a–f. Therefore, due to the negligible effect of SOC on the CB at equilibrium states of the Sb$_2$Mg$_3$ crystal structure, SOC will not have an effect on the band up to the critical tensile strain of the quantum phase transition. The band gap at equilibrium corresponding to the normal insulator can be tuned by applying tensile strain. Recent studies on 3D TIs have identified several materials with tunable topological phases.

Upon varying the hydrostatic tensile stress or strain parameters, these materials undergo a phase transition between a normal insulator and a nontrivial phase. Such transition may occur as a function of impurity doping, pressure, or temperature. Topological properties of Sb$_2$Mg$_3$ can be also changed by applying an external strain, thereby breaking the symmetry. The electronic band structures of Sb$_2$Mg$_3$ get altered as a result of increasing external strain, as shown in Figure 3a–e. We applied anisotropic strain in the range of $[-7.2\%, 7.2\%]$, tuning the band around the Γ point.

Figure 2. Bulk band structures of Sb$_2$Mg$_3$, calculated using (a) PBE and (b) hybrid Heyd–Scuseria–Ernzerhof (HSE) functionals at the equilibrium state.

Figure 3. Effects of (a) $-7.2\%$, (b) $-4.5\%$, (c) 0%, (d) 3.2%, (e) 4.5%, and (f) 7.2% strains on the band structures without SOC calculations. The bands zoom at the Γ point of anisotropic strain-induced Sb$_2$Mg$_3$. 

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(anisotropic strain is more reasonable than the xy-plane strain, as shown in Figure S4a–c). Not surprisingly, for Sb₂Mg₉ at the lower tensile strain, the material remains a normal insulator. Contrarily, the band gap increases monotonically as compressive strain is applied. Hence, the band gap reduction was achieved with increasing tensile strain.

From the partial orbital projection, the s, pₓ, and pᵧ orbital order from the CBM to VBM near the Fermi level at the Γ point remains the same with the SOC, as shown in Figure 3f. This feature can also be found in BiAs₁⁸ and SiGeCH₃,²⁹ which is in good agreement with previous works. When ε = 7.2%, as presented in Figure 3f, Sb₂Mg₃ becomes gapless without SOC. Furthermore, s–p orbital band inversion takes place at the Γ point. The two pₓ,ᵧ bands touch each other at the Fermi level, as presented in Figure 3f, at ε = 7.2% without SOC, whereas the s band moves down to the VB region, resulting in pₓ,ᵧ, pᵧ and s orbital order. When SOC is included, the band structure of the stretched Sb₂Mg₃ reopened, as shown in Figure 4b.

![Figure 4. DFT-PBE bands are fitted by tight-binding models (a) without and (b) with SOC at ε = 7.2%. Note that red dotted lines show the TB and blue solid lines refer to DFT-PBE.](image)

As discussed above, at ε = 7.2% without the effect of SOC, the VB has major Sb-pₓ,ᵧ and Sb-pᵧ orbital contribution, whereas the CB mainly is dominated by minor Sb-pₓ,ᵧ orbitals, as shown in Figure S3f. When the SOC occurs, the band degeneracy is lifted as a result of lack of inversion symmetry, and therefore, a global indirect band gap is generated. At a critical tensile strain of 7.2%, Sb₂Mg₃ undergoes a transition from a trivial phase to nontrivial phase. The band inversion of the opposite parities near the Γ point clearly indicates that the resulting state is a topological insulator. The states near the Fermi level are mainly dominated by pₓ,ᵧ orbitals, although the s and pₓ orbitals are removed from the Fermi level as a result of saturation, known as the orbital-filtering effect.⁴₃–⁴₆ Noticeably, the SOC effect plays two crucial roles in the phase change, namely, nontrivial gap opening and the band inversion between pₓ,ᵧ orbital states, which are observed in Sb₂Mg₉, as presented in Figure 4a,b. The TB models at ε = 7.2%, as illustrated in Figure 4a,b, without and with SOC respectively agree with the PBE value. For applications based on spintronic device technology, tunability of the spin splitting by the SOC effect and application of strain have been realized in many materials. Large spin splitting occurs along high-symmetry directions, and a typical Rashba effect is observed at the Γ point.⁷,⁴₆

Since the Bi₃Se₃ family has inversion symmetry, the topological invariant can be easily calculated by the parity product as guiding principles at high-symmetry points in the BZ.¹⁰ The topological nature of anisotropic strain-induced Sb₂Mg₃ is determined by calculating the Z₂ topological invariant using a tight-binding model. For a lattice with inversion symmetry, the Z₂ index can be concluded from the insight into the WCC, as performed using the Z₂ pack. The phase change in Sb₂Mg₃ is achieved by calculating the topological invariant on the basis of the U(2N) non-Abelian Berry connection predicted by Yu and co-workers.⁴⁹ Each of the nth occupied bands is indexed by ln kₓ, kᵧ), and square matrix F(kₓ, kᵧ) containing overlap integers is defined as

\[
F(kₓ, kᵧ) = \begin{pmatrix} n & kₓ, kᵧ \end{pmatrix}
\]

The unitary square complex can be solved as

\[
D(kᵧ) = \prod_{j=0}^{Nₓ-1} F(jΔkₓ, kᵧ)
\]

where \( Δkₓ = \frac{π}{Nₓ} \) represents the discrete spacing of \( Nₓ \) points along the kₓ direction. \( D(kᵧ) \) is a \( 2N \times 2N \) matrix that has 2N eigenvalues

\[
\lambda_{m}^{D}(kᵧ) = \left\{ \begin{array}{ll} 2 \times \mu \left( \theta_{m}(kᵧ) \right), & m = 1, 2, ..., 2N \\ \end{array} \right.
\]

where \( \theta_{m}(kᵧ) \) is the phase of the eigenvalues

\[
\theta_{m}(kᵧ) = \text{Im}[\log \lambda_{m}^{D}(kᵧ)]
\]

The Z₂ topological invariant is determined by counting the number of crossings between any arbitrary horizontal reference line, and the evaluation of the WCC along any direction in k space corresponds to the change in the phase factor \( \theta \) of the eigenvalues of the position operator projected onto the occupied subspace. The odd number of crossings of any random horizontal reference line in the case of \( kₓ = 0 \) with the presence of SOC, but for \( kₓ = 0.5 \) (i = 1, 2, 3) with the evolution of \( \theta \) is characterized by a Z₂ = 1 topological insulator. The horizontal reference line indicates the odd number of crossings, as shown in Figure 5a–c.

![Figure 5. Evolution lines of Wannier centers for Sb₂Mg₃ along (a–c) kₓ = 0.0, Zₓ = 1, and i = 1, 2, 3. (d) Momentum-resolved surface density of states subject to tensile strain of 7.2%.](image)

confirming that Sb₂Mg₃ is a topological insulator (Z₂ = 1: (111)) at ε = 7.2% with the presence of SOC, but for \( kₓ = 0.5 \) (i = 1, 2, 3), the evolution lines never cross the reference line (normal insulator, Z₂ = 0), as plotted in Figure S5b,d,f.

To explicitly show the nontrivial topological phase features of the surface states, we design an effective TB model on the basis of s, pₓ, pᵧ, and pₓ,ᵧ orbitals and obtained the low-energy spectrum of Sb₂Mg₃ by including the SOC interaction, as shown in Figure 5d. The tight-binding model based on the
maximally localized Wannier functions (MLWFs) correctly reproduces the DFT band structures and simulates the ARPES with the calculated surface density of states. The surface densities of states with SOC are performed using an iterative Green function method.

We notice that, out of all the bulk degrees of freedom, only the surface states inherit the electron spin. Energy dispersion in two dimensions at $\varepsilon = 7.2\%$ is shown in Figure 5d. Analogous to the gapless edge states, the spins of the surface carrier are locked to the direction of its momentum. The surface state occurs in the middle of the gap between the bulks and has a Dirac-like dispersion. The presence of topological surface states is a substantial property of a topological insulator having an insulating surface at ambient condition. Not only does it serve as a strong evidence of the nontrivial topology, it also serves directly as a bridge to the experiments.

Since the discovery of nontrivial topology, looking for new topological insulators has led to the search for binary heavy elements based on small-energy-gap semiconductors. Herein, we propose one of the simplest ways to realize a binary heavy element based on a closed-shell semiconductor with an alkaline earth element.\(^{5,17,44,50,51}\) Investigations on Dirac materials are very interesting for quantum property studies. Similarly, studies of stanene functionalized films,\(^{52,53}\) NbO$_2$Ta,\(^{44}\) 2D Mn-cyanogen,\(^{55}\) and Bi/Sb (111) films\(^{56}\) are in good agreement with previous studies. We believe that our findings will not only encourage existing experimental investigations but also pave the way toward constructing a periodic table of topological materials. Experimentally, a large strain may be difficult to achieve using traditional substrate engineering. Nevertheless, the strain of 7.2% was applied in Sb$_2$Mg$_3$; in principle, one can easily realize a topological insulator in future experiments.

3. CONCLUSIONS

In summary, topological phase transitions in Sb$_2$Mg$_3$ based on tensile strain is studied on the basis of density functional theory calculations. Upon inducing tensile strain, Sb$_2$Mg$_3$ is shown to be a topological phase transition at $\varepsilon = 7.2\%$ with SOC, creating an inverted band order. There is also transition from a normal insulator to the Dirac semimetallic state without SOC at critical tensile strain. These interesting results make Sb$_2$Mg$_3$ a promising candidate material for achieving a quantum spin Hall (QSH) insulator at room temperature.

4. COMPUTATIONAL METHODS

The electronic structure calculations are performed using density functional theory (DFT) by using the Vienna ab initio simulation package (VASP) code.\(^{57}\) The core ion/electron was obtained using projector-augmented wave (PAW)\(^{58}\) potential, and the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional was used.\(^{59,60}\) The relativistic effects were included in the calculations with a plane-wave basis kinetic energy cutoff of 400 eV, and the BZ was sampled by using a $5 \times 5 \times 5$ Monkhorst-Pack k-grid. The structure after the application of strain was fully relaxed up to the convergence of forces being less than 10$^{-5}$ eV per unit cell and 0.005 eV Å$^{-1}$ atomic position and cell parameters, respectively. The band structures were calculated with and without SOC\(^{55}\) being applied in the self-consistent field (SCF). The hybrid Heyd-Scuseria-Ernzerhof (HSE) functional with 25% of the short-range exact exchange is used to account for the under-estimation of the band gap for the PBE functional.\(^{61}\) Phonon dispersion is performed using the PHONOPY\(^{62}\) code combined with the DFT method in VASP. The topological invariant identified by the $Z_2$ number was determined by the method of WCC performed in a $Z_2$ pack.\(^{63}\)

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b00613.

Molecular dynamics (MD) simulations at 300 and 500 K, band structures of Sb$_2$Mg$_3$ at the equilibrium state without and with the SOC effect, orbital contributions in the band structures at different tensile strains without SOC, and evolution of WCCs (PDF)

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Notes

The authors declare no competing financial interest.

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