Modulation of Weyl semimetal state in half-Heusler GdPtBi enabled by hydrostatic pressure

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Keywords: Weyl semimetal, GdPtBi, hydrostatic pressure, electronic state transition

Abstract

The excitation of Weyl semimetals obeys the relativistic Weyl equation and attracted significant research attention due to its unique electronic state. In this paper, we present an emerging approach for modulating the electron state of half-Heusler GdPtBi by hydrostatic pressure. Through measurements of the temperature-dependent resistivity and magnetoresistance (MR), a phase transition from a Weyl semimetal to a semiconductor state was identified at about 2.0 GPa upon increasing the hydrostatic pressure. Electron transport in semiconductive GdPtBi is found to be well describable by Mott variable-range-hopping. The simulated electronic structures under different hydrostatic pressures further indicate that changes in the electronic states of atoms in the primary unit cell result in a phase transition in GdPtBi. This work presents an effective strategy for modulating the electronic state by tuning the lattice constant.

1. Introduction

Weyl/Dirac semimetals are a family of quantum materials that recently attracted great attention, particularly with the discovery of topological characters in materials such as TaAs [1, 2], Cd3As2 [3, 4], WTe2 [5, 6], ZrTe5 [7, 8], and Na3Bi [9, 10], among others. Generally, the energy bands of Weyl semimetals disperse linearly around the Weyl points, which can be viewed as magnetic monopoles in momentum space and described by the relativistic Weyl equation [11, 12]. Moreover, the Weyl points always appear in pairs with distinct chirality and are topologically stable against small perturbations due to topological protection. Hence, these topological electronic structures enable materials to exhibit broad potential applications and exhibit many novel phenomena, including chiral anomalies, topological surface states, Fermi arcs, and nontrivial Berry phases [3, 5, 8, 10]. Thus, creating and tuning the topological Weyl semimetal state of a material is an important topic in condensed-matter physics and materials science.

The diversity of half-Heusler compounds in compositions (i.e. XYZ, X, and Y are transition or rare earth metals and Z is the main-group element) provides great opportunities for tuning the band structure to realize topological properties [13–16]. In particular, half-Heusler compounds, such as GdPtBi, were verified as candidate Weyl semimetals [17]. This discovery opens the possibility of investigating the giant planar Hall effect [18], anomalous Hall effect [19], negative magnetoresistance (MR) [18], and other exotic phenomena [20, 21] in half-Heusler compounds. Recently, experiments and theories indicated that hydrostatic pressure is an efficient approach for tuning the electronic structures of topological materials [22, 23]. For example, high pressure can induce disruption of the semimetal state and a transition from...
New J. Phys. 23 (2021) 083041  
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semimetal to superconductivity in ZrTe$_5$ [23], while a topological transition from a semiconductor to a Weyl semimetal phase can occur in black phosphorous at moderate pressure [24]. Moreover, the large MR in WTe$_2$ can be modulated by pressure [22]. This is because the sizes of electron and hole pockets or other electronic states can be modulated by pressure. However, the Weyl physics of the half-Heusler GdPtBi under hydrostatic pressure has yet to be reported.

In this study, we introduce a hydrostatic pressure-based strategy for modulating the Weyl semimetal state of GdPtBi. We identify a phase transition from the Weyl semimetal to the semiconductor state at about 2.0 GPa upon increasing the hydrostatic pressure based on measurements of the temperature-dependent resistivity and MR. We find that in the semiconductor state, electron transport in GdPtBi can be well described by Mott variable-range-hopping theory. Moreover, the calculated energy-band and crystalline structures of GdPtBi under different hydrostatic pressures indicate that the change of the electronic states of atoms in the primary unit cell is the origin of this electronic-state transition. This work not only explores the underlying physics of the properties of GdPtBi, but also presents an efficient strategy for modulating its electronic state.

2. Methods

GdPtBi single crystals were grown by a Bi-flux method in which the high-purity raw materials of Gd (ingot, 99.99%), Pt (ingot, 99.99%), and Bi (ingot, 99.99%) were mixed with a molar ratio of 1:1:20 in an alumina crucible. Then, the crucible and mixture were sealed inside a tantalum tube in a glovebox filled with Ar, which was then sealed into an evacuated quartz tube. At that point, the quartz tube was thermally treated in a furnace as follows; the temperature was increased from room temperature to 1150 °C over 10 h and then maintained at 1150 °C for 48 h; subsequently, the temperature was slowly cooled to 650 °C at a rate of 2 °C h$^{-1}$. Finally, the excess of the Bi flux was removed by centrifuging the tube at 650 °C, giving rise to pure GdPtBi single crystals.

The crystal structures and chemical compositions of the GdPtBi single crystals were analyzed using a transmission electron microscope (TEM, FEI Titan Cs probe). The TEM lamellas were prepared with a focused ion beam in a scanning electron microscope (FIB/SEM, FEI Helios G4 UX). The preparation recipes for TEM lamellas were the same for all the samples, in which the beam energy of the ions for polishing was kept as small as possible at the center region of the lamellas to reduce the damage to the sample.

The high-pressure electrical transport was measured on a GdPtBi single crystal, which was polished along the [111] direction first until a very thin slab with a thickness of 0.1 mm was obtained for the test. A high-pressure cell model (Quantum Design HPC-33) was used in electrical measurements and installed in a Quantum Design physical-property-measurement system. To obtain a deeper understanding of the experimental results, we numerically investigated the electronic properties of the samples under pressure using the density functional theory (DFT). The value of the lattice constant after relaxation is about 6.70 Å, which is well consistent with the XRD and high-resolution transmission electron microscopy (HRTEM) results. The cut-off energy was set to 500 eV. The Brillouin zone was sampled by a Monkhorst–Pack $k$-mesh of size $11 \times 11 \times 11$. The GGA + $U$ method was applied during our calculations to account for the Coulomb interaction, while the effective $U$ values were chosen as 2 eV for the Pt-5$d$ and Gd-4$f$ orbitals.

3. Results and discussion

Figure 1(a) shows an optical photograph of the synthesized GdPtBi single crystal, which exhibits a size of 2.0 $\times$ 1.3 $\times$ 0.5 mm$^3$ and a characteristic polyhedral shape with smooth surfaces. The XRD pattern of the GdPtBi single crystals (figure 1(b)) indicates a MgAgAs-type structure crystallized along the [111] direction. The temperature-dependent longitudinal resistivity $\rho_{xx}(T)$ was investigated in a four-probe configuration under zero pressure ($P$). As hydrostatic pressure was applied, the behaviors of the $\rho_{xx}(T)$ curves were dramatically changed (figure 1(c)), particularly the values of the $\rho_{xx}$ increased with increasing pressure at low temperatures. A similar behavior has been also observed in ScPdBi [16], LuPdBi [25], and $\beta$-Bi$_4$I$_x$ [26], etc. However, in some materials, an opposite trend was observed. For example, the external pressure reduced the resistivity and made the materials more metallic in FePS$_3$ [27], MoS$_2$ [28], Li$_{10}$(NH$_3$)$_3$Fe$_3$Se$_2$ [29] and carbonaceous sulfur hydride [21]. The different behaviors of the materials under the external pressure can be ascribed to the different responses of the materials to the external pressure, owing to their inherent properties, such as crystal structure, electron arrangement, spin-orbital coupling, energy band structure and more others. At zero and low pressure ($P \lesssim 1.5$ GPa), the $\rho_{xx}(T)$ curves show similar behaviors. The resistivity increases gradually with temperature, forming a broad peak in the range of
Figure 1. Variation of transport properties with pressure. (a) and (b) Optical image and XRD pattern of GdPtBi single crystal. (c) Temperature-dependence resistivity of GdPtBi single crystal under various hydrostatic pressures. (d)–(f) Transverse MR with \( H \parallel I \) for various pressures at \( T = 2 \) K, 20 K, and 50 K, respectively. The MR is defined as \( \text{MR} = \left( \rho(H) - \rho(0 \text{ T}) \right) / \rho(0 \text{ T}) \times 100\% \).

50–100 K. Then, it slowly decreases as the temperature increases further to 300 K. Similar \( R - T \) behaviors have been found in other Dirac/Weyl semimetals materials, such as Cd\(_3\)As\(_2\) [30], ZrTe\(_5\) [7] and Na\(_3\)Bi [10], which should correlate with the carrier density near the Fermi level. Thus, the broad peak shift can be ascribed to the band structure regulation by hydrostatic pressure. However, when the pressure was increased to 2.0 GPa, the overall behavior of the \( \rho_{xx}(T) \) curve changed dramatically to that of a semiconductor-like material. The resistivity increased greatly with increasing pressure in the low-temperature range (roughly \( T \leq 100 \) K), but it remained nearly pressure independent between 100 and 300 K. The induced semiconductor behavior of the GdPtBi observed here is similar to that observed in the half-Heusler ScPdBi [16] and ScNiBi [31] under external pressures equal to or greater than 2.0 GPa. Note that the resistivity fluctuation around 10 K should be related to the antiferromagnetism of GdPtBi, and the same resistivity fluctuation phenomena were also observed when \( P < 2 \) GPa (the inset of figure 1(c)) and in literature [19].

As is well known, one of the most important signatures of the Weyl semimetal state is the observation of an negative MR (NMR) [32, 33] when the external electric and magnetic fields are parallel. To explore the Weyl-semimetal state of GdPtBi and the variation of the electronic state under pressure, we performed MR measurements of the GdPtBi single crystal with \( B \parallel I \parallel [110] \) at temperatures of 2 K, 20 K, and 50 K, respectively. We observed two salient features in the MR curves shown in figures 1(d)–(f); first, we observed a significantly large NMR (larger than -50%) at zero and low pressure (0 \( \leq P \leq 1.5 \) GPa). This NMR originates from charge pumping between two Weyl nodes [3] and demonstrates the topological stability of the Weyl semimetal state against weak perturbation. In addition, a cusp-like feature at a low magnetic field can be observed, which can be ascribed to the weak anti-localization (WAL) effect [34]. The coexistence of WAL effect and NMR phenomenon was also observed in Bi\(_{0.97}\)Sb\(_{0.03}\) [33], TaAs [35], TaP [36], and other topological materials, which further supports the existence of Weyl Fermions. For \( P \geq 2.0 \) GPa, positive and much larger (100%–150%) MRs appeared at various temperatures and pressures, indicating a transition from the Weyl semimetal state to a trivial semiconductor state with mobility change of carriers. Second, the influence of pressure on the MR increased with increasing temperature. At 2 K, the MR curves depend only weakly upon the pressures for both the Weyl semimetal state and the trivial semiconductor state; however, at 50 K, the MR depends strongly upon the pressures in both states. The consistency between the temperature-dependent resistivity and MR confirms that the Weyl semimetal state in a GdPtBi single crystal has been modulated by external hydrostatic pressure.

The low-temperature resistivity behavior of a GdPtBi single crystal under various hydrostatic pressures was studied further to understand the underlying physics, because low-temperature carrier-transport mechanisms are generally used to probe the intrinsic electron states of materials. Note that, at low temperatures and low pressures (figure 1(c)), the temperature-dependent resistivity curves of the GdPtBi single crystal exhibit metallic behavior. The conduction mechanism can be ascribed to the directional...
movement of electrons in the topological Weyl-semimetal state [5, 17]. A pressure-induced electronic-state transition from a Weyl semimetal to a semiconductor occurred in GdPtBi when \( P \geq 2.0 \) GPa. The carrier transport in a semiconductor can be attributed to electron hopping, which may be dominated by one of the following mechanisms: nearest-neighbor hopping, Efros–Shklovskii (ES) variable-range hopping, or Mott’s variable-range hopping [37, 38]. The differences between the nearest-neighbor and variable-range hopping mechanisms [38] in materials are illustrated in figure 2(a). Mathematically, they can be readily distinguished by the exponent \( s \) in the exponential temperature dependence of resistivity:

\[
\rho(T) = \rho_0 \exp \left[ - \left( \frac{T_0}{T} \right)^s \right],
\]

where

\[
T_0 = \frac{\beta}{kg(\mu)a^2}
\]

and the prefactor \( \rho_0 \) is determined based on the material properties. The parameters \( g(\mu) \), \( a \), and \( \beta \) are the density of states at the Fermi level, the localization states near the Fermi level, and a numerical coefficient, respectively. Exponent \( s \) is a constant related to the electron density near the Fermi level; its value distinguishes the hopping mechanism in the material. The exponents \( s = 1 \), \( s = 1/2 \), and \( s = 1/4 \) correspond to nearest-neighbor hopping, ES variable-range hopping, and Mott’s variable-range hopping, respectively. The longitudinal resistivity in GdPtBi was fitted by using \( s = 1 \), \( s = 1/2 \), and \( s = 1/4 \) according to equation (1) when \( P \geq 2.0 \) GPa (figures 3(b)–(d)). The fitting quality was evaluated by the residual sum of squares listed in the brackets in figures 3(b)–(d). We find that the \( R-T \) curves can be better fitted using \( s = 1/4 \) rather than \( s = 1 \) or \( s = 1/2 \). This result indicates that conduction is dominated by Mott variable-range hopping, which is very different from the metallic-like behavior in the topological Weyl semimetal state. Thus, the changes in the carrier transport mechanism further demonstrate that the electronic states were changed in the GdPtBi single crystal under hydrostatic pressure.

We experimentally observed that the electronic state of GdPtBi transforms from a topological Weyl semimetal state to a semiconductor-like state when the applied hydrostatic pressure reaches 2 GPa. Normally, a change in the electronic state of a material can be caused by a decomposition and/or structural

Figure 2. Variation in the carrier-hopping mechanisms with pressure. (a) Schematic hopping-transition mechanisms in semiconductors, where the dashed line is the Fermi level, the red balls are the occupied states, and the solid lines are the unoccupied states. (b)–(d) Resistivity of GdPtBi when \( P \geq 2.0 \) GPa is fit to equation (1) with \( s = 1 \), \( s = 1/2 \), and \( s = 1/4 \), respectively. The residual sum of squares fittings is listed in brackets.
phase transition due to an external stimulus, such as a change in temperature or pressure. In this study, we focus on the application of high hydrostatic pressure. Therefore, we studied a single crystal using HRTEM before and after applying such pressure. From the high-resolution lattice images along the [100]-zone axis (figures 3(b) and (c)), we find that the GdPtBi samples exhibit a single crystal and no second phase exists before or after applying pressure. Additionally, the lattice patterns are identical in figures 3(b) and (c); these observations indicate that the GdPtBi single crystal did not decompose during application of pressure, unlike the bismuth binary compounds (i.e. BiI₄), which decomposed into Bi/BiI₃ [26]. The non-decomposition of the material was reconfirmed by energy-dispersive x-ray (EDX)-composition analysis at different points. These results indicate that the single crystal experienced only an elastic deformation/strain under hydrostatic pressure up to 2.5 GPa (the maximum pressure we can apply in our lab). We find that the molar ratio of Gd:Pt:Bi is about 32.7:34.0:33.3 based on the EDX data (figure 3(c)); these values are close to the ideal stoichiometry of GdPtBi. From the HRTEM images, we also found that the GdPtBi single crystal exhibits a cubic structure belonging to the \( Fm3m \) space group and that the Gd, Pt, and Bi atoms occupy the Wyckoff 4b, 4c, and 4a positions (figure 3(d)), respectively. The HRTEM images and EDS data well confirm that the pressure-dependent transport properties observed here originate from the Weyl transport to Mott’s variable-range hopping transport, not from the poor quality of GdPtBi crystals. Based on the above analysis, we conjecture that shrinkage of the lattice (elastic formation) should be the dominant factor for the electronic state transition in GdPtBi crystal; this is reasonable because elastic deformation can be triggered by high pressure from all angles, leading to a varied electronic state of GdPtBi, as interpreted by the model in figure 3(d). First, GdPtBi is a zero-gap semimetal under zero magnetic field and pressure, while the Weyl nodes can be generated by Zeeman energy. Then, the valence and conduction bands can be separated from each other due to the compressed lattice constant with increasing hydrostatic pressure, resulting in a transition from Weyl semimetal to a semiconductor state. This conjecture was confirmed by numerical experiments.

The influence of hydrostatic pressure upon the band structure of single crystal GdPtBi was studied numerically using DFT methods [25]. As expected, hydrostatic pressure directly decreases the lattice constants of GdPtBi. Figure 4 shows the calculated electronic band structures of GdPtBi when the lattice constant was decreased under hydrostatic pressure. We find that GdPtBi is a semimetal at ambient pressure, where Weyl nodes can be generated easily in a magnetic field due to the Zeeman energy (figure 4(a)). The clear band-inversion signature indicates the nontrivial semimetal state. We find that no obvious change is present in the band structure of GdPtBi when the lattice constant varies by less than \(-0.3\%\) (figures 4(a)–(c)). A direct bandgap appears at the \( \Gamma \) point between the conduction and valence bands.
when the lattice constant declines by 0.4%, indicating the occurrence of a topological phase transition in figure 4(d). In particular, the bandgap increased in figures 4(d)–(f) when the lattice constant decreased under increasing pressure. This strongly supports our conjecture in figure 3(d), where the valence and conduction bands in GdPtBi were separated gradually by hydrostatic pressure due to lattice constant shrinkage. These numerical data are consistent with the experimental results in figures 1 and 2, demonstrating the tunability of the Weyl semimetal state in GdPtBi single crystals subject to hydrostatic pressure.

4. Summary

In summary, we observed a transition from the Weyl semimetal to the semiconductor state in GdPtBi single crystals upon the application of hydrostatic pressure. The transverse resistivity and MR data indicate that the transition occurs at 2.0 GPa. The calculated electronic band and crystalline structures of GdPtBi under different hydrostatic pressures indicate that the change of the electronic state in the basic unit of the crystalline structure is the cause of the state transition. This work not only explores previously unrevealed properties of GdPtBi but also presents an efficient strategy for modulating its electronic state by tuning its lattice constant.

Acknowledgments

This work was financially supported by the King Abdullah University of Science and Technology (KAUST) Office of Sponsored Research (OSR), Saudi Arabia, under Award No. CRF-2015-2549-CRG4, and the China Postdoctoral Science Foundation No. Y6BK011M51. JLZ acknowledges the financial support from the National Natural Science Foundation of China (No. 11974150). WHW acknowledges support from the National Natural Science Foundation of China (No. 11974406) and Fujian Innovation Academy, Chinese Academy of Sciences.

Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.
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