Heavy-atom antiferromagnet GdBiTe: an interplay of magnetism and topology in a symmetry-protected topological semimetal

Supporting Information

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1. Summary of the attempts to synthesize GdBiTe$_3$

To obtain GdBiTe$_3$ we initially followed the strategies reported in [15–17]. Solid-state reactions between Gd$_2$Te$_3$ and Bi$_2$Te$_3$ taken in a molar 1:1 ratio and annealed at various temperatures within the 600–850 °C range yielded multi-phase mixtures of GdTe$_{2-x}$, Bi$_2$Te$_3$ and Bi-richer tellurides, likely BiTe. Starting mixtures of Bi$_2$Se$_3$ and Gd$_2$Te$_3$ annealed at 950 °C provided a similar outcome. Accordingly, DSC studies of the stoichiometric Gd$_2$Te$_3$ and Bi$_2$Te$_3$ mixtures cycled up to 800 or 950 °C and back down to room temperature showed only the melting signal of bismuth telluride(s) at 582 °C (heating curve) and 584 °C (cooling curve). Besides, a small portion of Gd$_2$Te$_3$ likely reacted with the quartz walls producing Gd$_2$TeO$_2$ as detected in the powder X-ray diffraction (PXRD) patterns. In addition, growth from KI flux was attempted by slow cooling at the rate of 2 K/min from 850 °C down to 375 °C, resulting in Bi$_2$Te$_3$ and BiTe in form of small crystals and melting beads. The Gd was bound in more or less amorphous powder. No change in the phase composition was observed after a long-term annealing of the starting GdTe$_{2-x}$ and Bi$_2$Te$_3$ (2:1 ratio) mixture.

Beside we tried multiple other synthetic routes starting from various reactants. Solid-state reactions of the stoichiometric mixtures of the elements led to the formation of Bi$_2$Te$_3$ and GdTe$_3$ at 270 °C, and of BiTe and GdTe$_{2-x}$ at 470 °C. A mixture of Bi$_2$Te$_3$ and GdTe$_3$ taken in 1:1 molar ratio was subjected to long-term annealing at 850 °C or 950 °C and was explored by thermochemical analysis. No reaction was observed, the PXRD after the treatment showed only the starting materials. Likewise, we observed no chemical reaction between GdTe$_2$ and Bi$_2$Te$_3$ taken in a 1:1 molar ratio. When GdTe$_2$ reacts with Bi at 950 °C for several days, a phase mixture of Bi$_2$Te$_3$ (and/or Bi-richer telluride), Gd$_2$Te$_3$ and bismuth is obtained. The respective DSC study shows the melting signals of Bi$_2$Te$_3$ at ca. 580 °C. Reacting GdTe$_3$ with Bi results in a mixture of GdTe$_2$ and BiTe.

Chemical transport reactions with iodine in various temperature gradients were performed. Unfortunately, transport of bismuth and gadolinium tellurides enhances in very different temperature ranges, e.g. while Bi$_2$Te$_3$ migrate most efficiently from 500 °C to 400 °C, GdTe$_2$ migrates from 900 °C to 800 °C Setting the temperature gradient somewhat between 500 and 800 °C we were able to grow BiTeI crystals only. Syntheses with GdCl$_3$ and Bi$_2$Te$_3$ mixtures with various annealing regimes did not result in any changes of the initial phase composition. Temperature gradients chosen between 450 and 600 °C favored the crystal growth of Bi$_2$Te$_3$.

2. Powder pattern
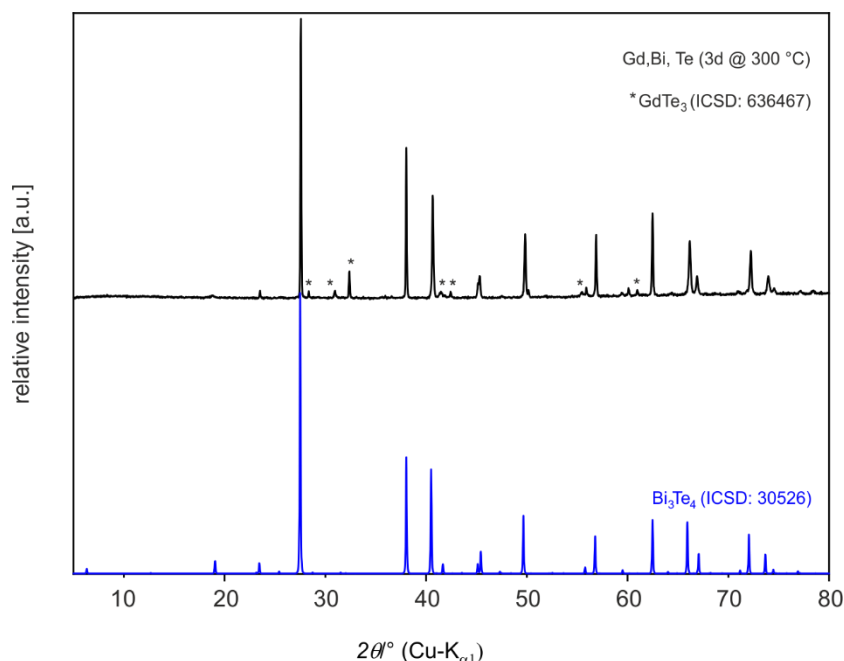
Figure S1. PXRD pattern of an equimolar mixture of Gd, Bi, Te annealed at 300 °C for 3 days. At this low temperature no ternary phase is formed.

3. Crystal Structure Elucidation of GdBiTe and LaBiTe

Table S1. Coefficients U_{ij} (in Å^2) of the tensors of the anisotropic displacement and equivalent isotropic displacement parameters for the atoms in GdBiTe. For all atoms $U_{23} = U_{13} = 0$. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

| Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{eq}
Gd1	0.00305(6)	0. 00305(6)	0.0036(1)	0	0.00324(5)
Bi1	0.00370(5)	0. 00370(5)	0.00471(8)	0	0.00404(5)
Te1	0.00285(7)	0. 00285(7)	0.0039(1)	0	0.00320(6)
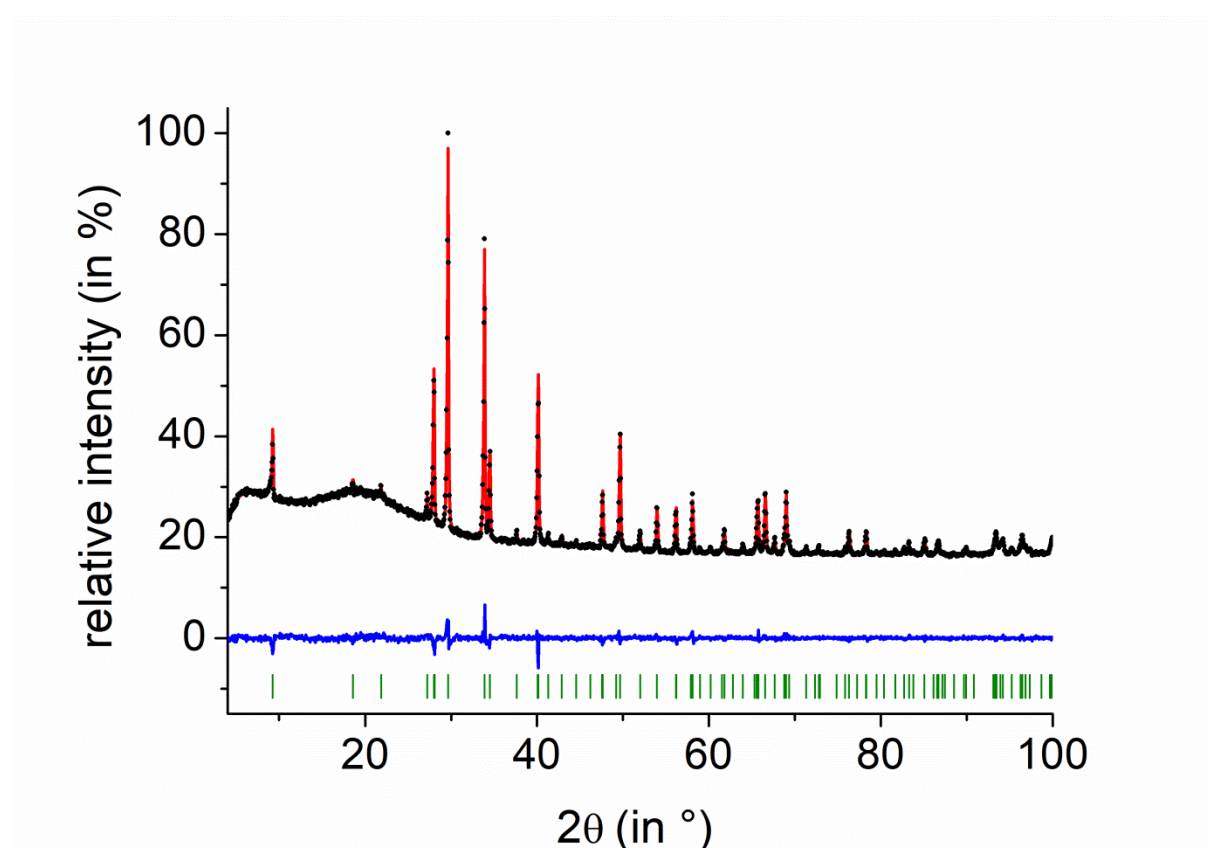
Figure S2. Rietveld refinement of LaBiTe (Huber G670 diffractometer, λ = 154.06 pm; R_{wp} = 1.63 %, GooF = 0.65, space group $P4/nmm$, R_{Bragg} = 1.70%, 31 parameters (thereof 18 background), a = 4.48814(9) Å, c = 9.5501(3) Å, V = 192.371 Å^3, ρ = 8.209 g cm^{-3}). The experimental data is depicted by black dots, the calculated diffraction pattern in red. The difference plot is drawn in blue. Vertical green lines show the position of the Bragg reflections.

z = 0.0
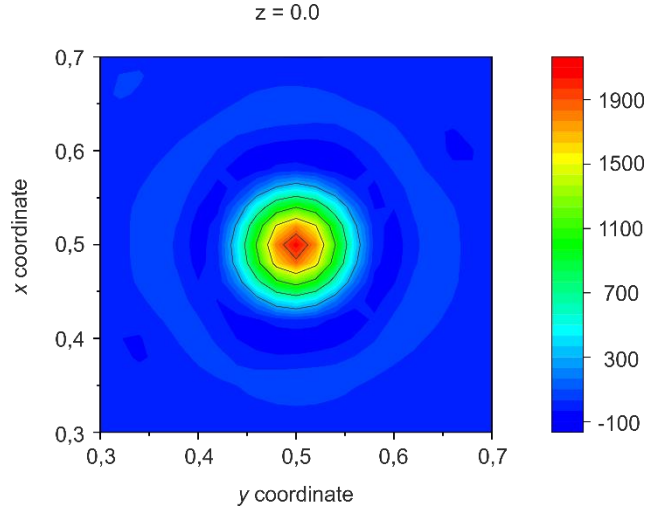
Figure S3. Fourier section around Bi1 in GdBiTe. The electron density is drawn in contour line steps of 400 eA^{-3}.

4. Wilson loop spectra and surface electronic structures of GdBiTe when $\vec{\mathcal{M}} \parallel z$

AFM-I, $\vec{\mathcal{M}} \parallel z$
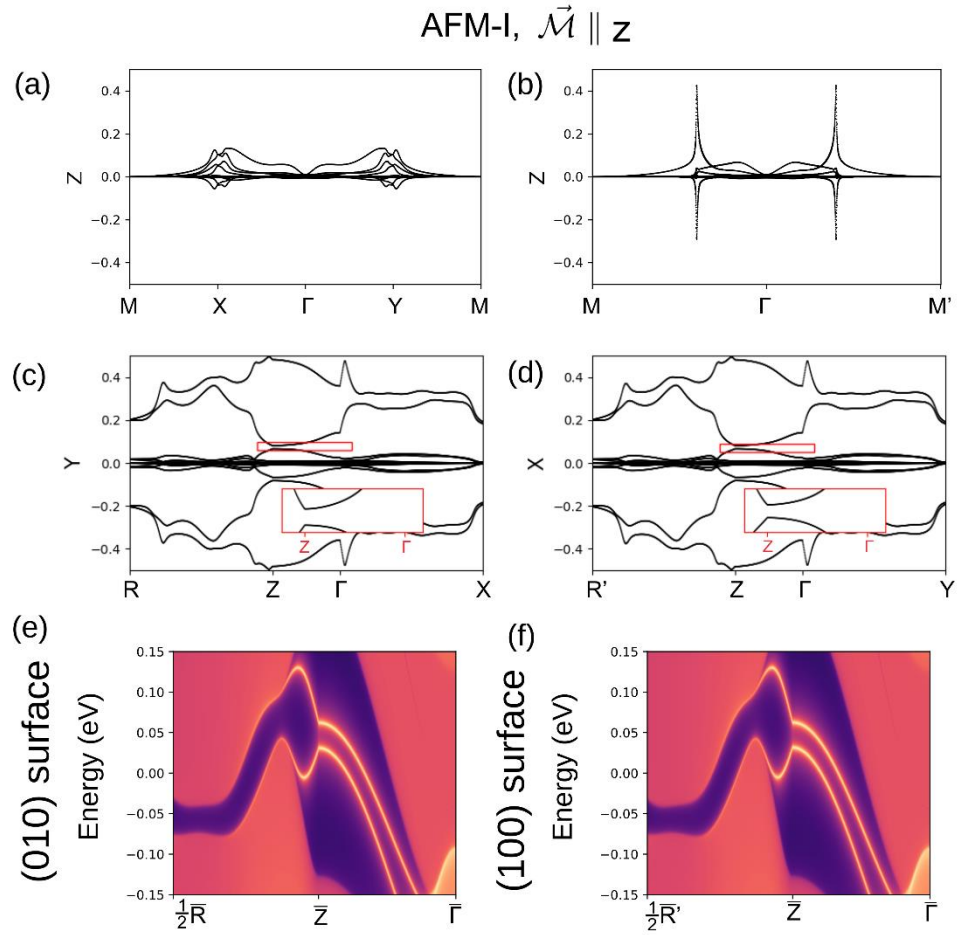
Figure S4. (a–d) Wilson loop spectra and (e, f) surface electronic spectra of the AFM-I antiferromagnetic phase with magnetic moments oriented out-of-plane.

5. Evolution of the GdBiTe bulk electronic structure as a function of the Hubbard parameter U

Magnetic properties of GdBiTe arise from the Gd f-electrons. According to our theoretical calculations, these electrons form two groups of almost flat bands in the valence and in the conduction parts of the band structure. These groups are localized at around -5.5 and 0.5 eV, respectively, at U=0 eV (Fig. S5). Close to the Fermi level, other electronic states do not hybridize with the f-states. An increase of the Hubbard parameter U leads to a downward (upward) shift in the energy of the valence (conduction) f-bands, respectively, without any changes in the dispersion of the other bands. As a result, the identified (topological) features and the conclusions made in the manuscript do not alter with the Hubbard parameter.
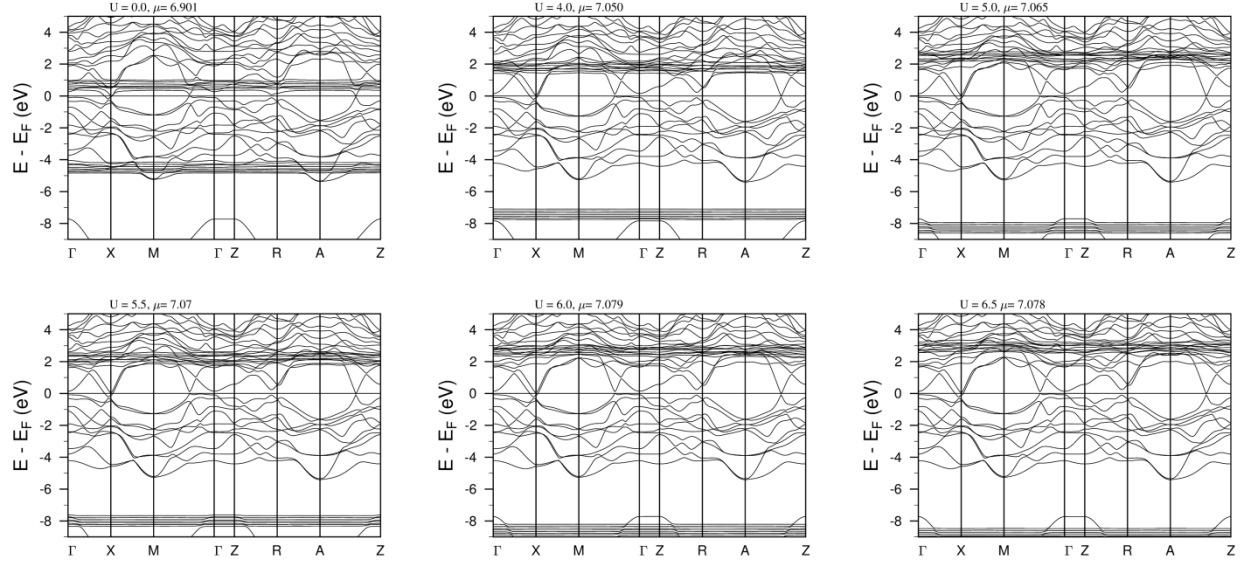
Figure S5. Bulk electronic structure of GdBiTe at various U. U – the Hubbard parameter, μ – the calculated magnetic moment (μ_B) per Gd atom.