Strain Tuning the Band Topology of Epitaxial GdSb Quantum Wells

Hadass S. Inbar¹*, Dai Q. Ho²,³&, Shouvik Chatterjee⁴#, Aaron N. Engel¹, Shoaib Khalid²†, Connor P. Dempsey⁴, Mihir Pendharkar⁴*, Yu Hao Chang¹, Shinichi Nishihaya¹†, Alexei V. Fedorov⁵, Donghui Lu⁶, Makoto Hashimoto⁶, Dan Read⁶,⁷, Anderson Janotti², Christopher J. Palmstrøm¹,⁴*¹

¹Materials Department, University of California Santa Barbara, Santa Barbara, CA 93106, USA
²Department of Materials Science and Engineering, University of Delaware, Newark, DE 19716, USA
³Faculty of Natural Sciences, Quy Nhon University, Quy Nhon 59000, Vietnam
⁴Electrical and Computer Engineering Department, University of California Santa Barbara, Santa Barbara, CA 93106, USA
⁵Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA
⁶Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratory, CA, USA
⁷School of Physics and Astronomy, Cardiff University, Cardiff CF24 3AA, UK
&These authors contributed equally

* Email: hadass@ucsb.edu (H.S.I.), cjpalm@ucsb.edu (C.J.P.)

(Dated: November 27, 2022)

KEYWORDS: topological materials; rare-earth monopnictide, strain; angle-resolved photoemission spectroscopy; molecular beam epitaxy.
**ABSTRACT:**

Rare-earth monopnictide (RE-V) semimetal crystals subject to hydrostatic pressure have shown interesting trends in magnetoresistance, magnetic ordering, and superconductivity, with theory predicting pressure-induced band inversion. Yet, thus far, there have been no direct experimental reports of interchanged band order in RE-Vs due to strain. This work studies the evolution of band topology in biaxial strained GdSb (001) epitaxial films using angle-resolved photoemission spectroscopy (ARPES) and density functional theory (DFT). We find that biaxial strain continuously tunes the electronic structure from topologically trivial to nontrivial. Compressive biaxial strain eliminates the gap between the hole and the electron bands dispersing along the [001] direction. Using a simple tight-binding model accounting for the orbital symmetry of each band, we reproduce trends seen in DFT calculations and ARPES measurements and elucidate the origin of conduction and valence band shifts. Finally, we discuss the effect of biaxial strain on carrier compensation and magnetic ordering temperature.
Strain engineering of low-dimensional topological quantum materials serves as a powerful approach to manipulating the electronic band structures, thereby controlling topological phase transitions and transport behavior\(^1\). For example, strained HgTe quantum wells grown in the tensile and compressive regimes were shown to transition from a semimetallic to a two-dimensional topological insulator (TI) system, respectively\(^2\). Despite the promise of topological state tuning, strain studies of quantum materials thin films are typically restricted either to local, defect-induced strain gradients\(^3-5\) or to strain levels below 1\% strain\(^6,7\) in the case of uniform strain in lattice-mismatched growths. In TIs such as the group V-chalcogenides (\(X_2Z_3, X=\text{Bi, Sb} ; Z=\text{Te, Se}\)), unstrained growths occur even on substrates with high lattice mismatch due to the low bonding energies between van der Waals layers\(^8,9\). In addition to the challenge of stabilizing highly strained pseudomorphic topological materials, visualizing the band structure modifications as a function of strain/pressure has been difficult in both bulk single crystals and thin films. In single crystals, large pressure cells are difficult to implement, and when using mechanical strain tuning apparatus special care is needed to ensure the application of uniform strain\(^10-13\). For thin films, there are limited reports combining strained film growth with direct spectroscopic tools such as angle-resolved photoemission spectroscopy (ARPES), with a few exceptions in oxide films\(^14,15\).

Here, we use ARPES to study the evolution of the electronic structure of GdSb thin films grown by molecular beam epitaxy (MBE) subject to 2\% tensile and 2\% compressive biaxial strain. GdSb belongs to the rare-earth monopnictide (RE-V) family of compounds and is particularly interesting due to the relatively small electron-hole band energy gap that can be inverted via attainable strain/hydrostatic pressure, resulting in a nontrivial \(Z_2\) topological invariant classification\(^16\). Recent reports of bulk RE-V crystals under hydrostatic pressure reveal the emergence of a superconducting phase transition in nonmagnetic RE-Vs\(^17-19\), and theoretical predictions suggest potential strain and pressure-induced
transition in band topology\textsuperscript{16,20–23}. In addition to observing a strain-driven topological phase transition in the RE-V system, strain studies of RE-Vs are highly relevant for spintronic-based applications as another control knob that can be used to tune magnetoresistance and magnetic properties in RE-V thin films. GdSb thin films present high magnetoresistance\textsuperscript{24}, have a type-II antiferromagnetic ordering at nearly the highest temperature of all RE-V (\(T_N = 24\) K)\textsuperscript{25}, and can be epitaxially integrated with III-V compounds (see Figure 1(a-c))\textsuperscript{26}. GdSb also has a lattice parameter of \(a = 6.219\) Å between InSb (6.479 Å) and GaSb (6.096 Å)/AlSb (6.136 Å), allowing high tensile and compressive biaxial strain by varying the underlying semiconducting III-V buffer layer structure as shown in Figure 1(d). Finally, coupled with III-V compounds, RE-V thin films and particles have shown many potential device applications\textsuperscript{27}, including buried metallic contacts\textsuperscript{28}, THz emitters and detectors\textsuperscript{29,30}, thermoelectrics\textsuperscript{31,32}, plasmonic heterostructures\textsuperscript{33}, and diffusion barriers\textsuperscript{34}. Therefore, straining RE-V thin films presents another avenue to tune the functional properties of these semimetals, specifically by modifying magnetic exchange interaction and the charge carrier ratio in these otherwise electron-hole-compensated semimetal systems.

MBE was used to grow epitaxial GdSb (001) thin films on In\textsubscript{x}Ga\textsubscript{1−x}Sb/ In\textsubscript{x}Al\textsubscript{1−x}Sb buffer layers nucleated on a GaSb (001) substrate. For photoemission and scanning tunneling microscopy (STM) studies, p-type doped substrates and p-type In\textsubscript{x}Ga\textsubscript{1−x}Sb buffer layers were used. By changing the Al/In concentration in the buffer layer, the in-plane lattice parameter was adjusted before the GdSb growth, as shown in Figure 1(d). For magnetotransport measurements, undoped In\textsubscript{x}Al\textsubscript{1−x}Sb buffer layers and epi-ready semi-insulating GaSb (001) wafers were used. Further details on the GdSb growth window, ARPES measurement conditions, and electronic characterization of lattice-matched unstrained films are detailed in our previous report\textsuperscript{24}. The coherent growth of strained films was studied \textit{in situ} with reflection high-energy electron diffraction (RHEED), STM, and confirmed \textit{ex situ} with x-ray diffraction (XRD) measurements. We investigated the electronic structure of GdSb theoretically using density functional theory (DFT) and the screened hybrid functional of Heyd, Scuseria, and Ernzerhof (HSE06)\textsuperscript{35,36} with 25%
of exact exchange and accounting for spin-orbit coupling, as implemented in the VASP code\textsuperscript{37,38}. Additional details on the DFT calculations are provided in Supporting Information.

This work compares two extreme strain levels of GdSb films: 2\% compressive (−2\%) and 2\% tensile (+2\%) biaxial strain. To reduce thin-film contributions to the electronic band structure, such as substrate charge transfer and quantum confinement\textsuperscript{39}, highly strained films as thick as possible (i.e., near the critical relaxation thickness) are studied. In GdSb, strong film-substrate interactions and interlayer bonding allow pseudomorphic growth at high strain levels. The critical thickness ($h_c$) is determined empirically as the onset of partial relaxation observed with XRD reciprocal space maps (RSM), with $h_c = 5.5 \text{ nm}$ in 2\% compressively strained films. Consequently, all strained growths are limited to 4 nm in thickness. Grazing incidence RSM of the (226) reflections for 4-nm-thick GdSb films are shown in Figure 1(b-c), confirming that the layers remain pseudomorphically strained. From the RSM-extracted in-plane and out-of-plane GdSb lattice parameters, we calculated the planar ($\varepsilon_\parallel$) and vertical ($\varepsilon_\perp$) strains and Poisson’s ratio: $\varepsilon_\perp = \frac{-2\nu}{1-\nu}$\textsuperscript{40} such that $\nu_{\text{exp}} = 0.12 \pm 0.03$. The experimental Poisson’s ratio agrees with our DFT-calculated value $\nu_{\text{DFT}} = 0.10$ and is comparable to earlier predictions made for other RE-Vs\textsuperscript{41,42}. In \textit{in situ} STM scans of the 2\% compressive strained GdSb film grown directly on GaSb in Figure 1(e) and other GdSb films on ternary III-V buffers\textsuperscript{24} confirm the growth of a smooth and continuous GdSb film with terrace step heights consistent with half of a unit cell (one atomic monolayer).

The Fermi surface of GdSb is composed of two hole pockets (β and δ) at the Brillouin zone center (Γ), a third spin-orbit split-off band (γ) lying below the Fermi level, and three ellipsoidal electron pockets (α) at the Brillouin zone edge ($X_1, X_2, X_3$, the $X_3$ high-symmetry point transforming to the $Z$ high-symmetry point in the tetragonal $I4/mmm$ space group under biaxial strain). VUV-ARPES measurements were performed at the Advanced Light Source at beamline 10.0.1.2, and at the Stanford Synchrotron Radiation Lightsource at beamline 5-2 with additional details on measurement conditions provided in Supporting
Information. Figure 2(a-d) highlights the ARPES high-symmetry cuts studied for the electron pockets lying at \(X_{1,2}\) points in the film plane, and Figure 2(e-f) shows the electron pocket at \(Z\) positioned along the film plane normal. The two sub-band levels of the electron pocket seen for both strain levels in Figure 2(b) are due to quantum confinement, and additional valence band quantum wells are seen in Figure 3 (see Figure S1 for DFT calculations accounting for quantum size effects). The nearly identical number of quantum well sub-bands and similar energy splitting in the biaxially strained films confirm the growth of atomically uniform films of the same thickness and comparable interface potentials when grown on GaSb (\(\varepsilon = -2\%\)) and In_{0.65}Ga_{0.35}Sb (\(\varepsilon = +2\%\)) buffer layers. The effect of finite-thickness quantization on the band topology is addressed at a later stage. Scans of the electron pocket in Figure 2(d) present the minor axis cut along the ellipsoidal electron pocket but also show the projection of the major axis from an electron pocket in a neighboring Brillouin zone in Figure 2(b) due to the high \(k_z\) broadening expected for the VUV light used in the ARPES measurements\(^{43}\).

The DFT-calculated and ARPES-extracted Fermi wave vectors and band extrema positions for both strain values are summarized in Table S1, and the calculated gap at \(Z\), \(E_g(Z)\), between the conduction and valence bands as a function of strain level is shown in Figure 4(c). ARPES and DFT- extracted Fermi wave vectors and band extrema positions reported in Table S1 reveal that compressive strain widens the bandwidth of the hole and electron pockets, primarily along \(X - W\) and \(Z - W\) (see Figure 2(g-h)). ARPES of the electron pockets lying in the film plane at \(X_{1,2}\) (Figure 2(a-d)) shows the increased bandwidth upon compressive strain \((-2\%)\), with the band minima shifting from \(\alpha_{X_{1,2}}^{+2\%} = -0.375\) eV to \(\alpha_{X_{1,2}}^{-2\%} = -0.440\) eV. Along the semimajor axis in Figure 2(a-b), the Fermi wave vector noticeably increases with compressive strain. The hole band extrema in the film plane \(\delta_{X_{1,2}}^{+2\%} = -0.66\) eV, \(\beta_{X_{1,2}}^{+2\%} = -1.41\) eV and \(\delta_{X_{1,2}}^{-2\%} = -0.68\) eV, \(\beta_{X_{1,2}}^{-2\%} = -1.45\) eV (see also Figure 3) remain largely unchanged, in agreement with DFT predictions in Figure 2(g).
Our DFT calculations in Figure 2(g-h) show that at 2% compressive strain, GdSb transitions into a topological semimetal state as the hole and electron bands anti-cross along $\Gamma - Z$ and are inverted at $Z$, whereas the in-plane electron and hole bands at $X_{\pm,2}$ remain gapped. The ARPES dispersions for bands lying in the film plane are consistent with our DFT calculations and support the predicted band inversion scenario. Due to high $k_z$ broadening, the valence bands at $k_z=\Gamma$ also project to the $k_z=Z$ plane leading to a blurred background intensity preventing the extraction of the electron pocket minima at $Z$ from the raw plots or the observation of the expected topological surface states (TSS) for the compressively strained film (TSS in RE-Vs typically have a weaker spectral intensity compared to the bulk bands\textsuperscript{44,45}). However, by fitting the hole bands maximum at $Z$ along $W-Z-W$, we see a shift in the heavy-hole band upward from $\delta_{Z}^{\pm 2\%} = -0.9$ to $\delta_{Z}^{\pm 2\%} = -0.59$ eV and the light-hole band $\beta_{Z}^{\pm 2\%} = -1.45$ to $\beta_{Z}^{\pm 2\%} = -1.31$ eV (see Table S1). The influence of epitaxial strain on the hole bands, primarily lying along $\Gamma - Z$ (and only small shifts for the bands dispersing in-plane), agrees with our calculations in Figure 2(g-h) and earlier DFT calculations performed for LaSb\textsuperscript{46}.

We have further checked the topological nature of the strained GdSb by evaluating the $\mathbb{Z}_2$ strong topological index $\nu_0$ according to the band parity product criteria\textsuperscript{47} considered at eight time-reversal inversion momenta (TRIM) points: $\Gamma$, 4 $L$, 2 $X$, and $Z$ where $(-1)^{\nu_0} = \prod_{i=1}^{8} \delta_i$, $\delta_i$ being the parity product at each TRIM point for all occupied bands. Time-reversal symmetry ($\Theta$) and primitive-lattice translation symmetry ($T_{1/2}$) in GdSb are broken, however their combination is preserved ($S=\Theta T_{1/2}$), enabling the classification of the topological nature using the $\mathbb{Z}_2$ topological invariant\textsuperscript{48}. In the unstrained and tensile cases, the $\mathbb{Z}_2$ invariant $\nu_0 = 0$, demonstrating a trivial topological state. In contrast, we observe a change in the parity product at the $Z$ point (from + to −) in the compressively strained case, resulting in a $\mathbb{Z}_2$ index $\nu_0 = 1$ which indicates a nontrivial topological band structure.
Next, we map the strain evolution of the valence band at the Brillouin zone center at $k_z=\Gamma$. Scans of the hole pockets along $\bar{M} - \Gamma - \bar{M}$ ($\Gamma - X_{1,2}$ in the bulk Brillouin zone) and $\bar{X} - \Gamma - \bar{X}$ ($\Gamma - K$ in the bulk Brillouin zone) in Figure 3 show multiple quantum well states and agree with the number of subbands seen in our DFT calculations in Figure S1 for films of the same thickness. As in earlier observations for LuSb$^{39}$ (a nonmagnetic RE-V analog), due to quantum confinement effects in the 4-nm-thick films, the Fermi surface area of the hole pockets and the electron pockets in the strained thin films is slightly smaller than the values extracted via ARPES for thicker unstrained GdSb films$^{24}$. The band extrema positions in the 4-nm-thick films (detailed in Table S1) are expected to be shifted to higher (lower) binding energies for the hole (electron) pockets compared to the DFT calculations in Figure 2(g-h) performed for bulk-like GdSb.

A modest change in the concentration of all charge carriers is seen as a function of strain (see our earlier work$^{24}$ for details on carrier density analysis). Overall, the charge carrier ratio increases with compressive strain from $\left(\frac{n_e}{n_h}\right)_{+2\%} = 1.52$ to $\left(\frac{n_e}{n_h}\right)_{-2\%} = 1.85$, suggesting that biaxial strain could serve as another degree of freedom to tune magnetoresistance in RE-Vs. The electron-rich carrier ratio measured for both thin films, deviating from exact compensation in unstrained bulk GdSb, agrees with our earlier studies of quantum confinement effects in RE-Vs$^{39}$.

The hole band Fermi wave vectors and $\gamma$ band extrema near the valence band in Table S1 (extracted from Figure 3 and Figure 2(f)) deviate from our DFT calculations, which predicted a displacement of the valence band maximum with strain (Figure 2(g-h) and Table S1), a trend we do not observe experimentally. In Figure 3, the hole split-off $\gamma$ band maximum at $\Gamma$ does not shift significantly with strain and remains at the same maximum energy of $-0.3$ eV. In addition, when transitioning from tensile to compressive strain we observe a decrease in $k_F$ along $\bar{M} - \Gamma - \bar{M}$ in contrast to DFT predictions. These two trends suggest that the observed position of the Fermi level in the compressive film could differ from
the initial DFT-calculated position shown in Figure 2(g-h). The origin of this variation between ARPES results and DFT calculations could be either due to quantum size effects in the hole band\textsuperscript{39}, related to the hydrostatic tensor contributions in the DFT-modeled valence band shift\textsuperscript{49}, or resulting from experimental effects such as defects in the compressively strained film leading to bulk doping or potential Fermi level pinning at the film surface. See Supporting Information for additional details on the DFT and ARPES values compared as a function of a rigid Fermi level shift.

The bands lying in the film plane normal direction, along [001] ($\Gamma - Z$), are primarily affected by epitaxial strain, whereas in RE-Vs under hydrostatic pressure \textsuperscript{16,21} all three $\Gamma - X$ high-symmetry directions are equivalent. The degree of valence and conduction band overlap in the axis along the film plane normal can be explained using a simple tight-binding (TB) model, accounting for the orbital composition of the electron and hole bands near the Fermi level and the change in the nearest-neighbor and next-nearest neighbor interactions scaling with strain (see Figure 4(b-c) and Supporting Information for details on the TB model). Based on the orbital-resolved DFT electronic band structure in Figure 4(a), we construct a TB model that reproduces well the DFT-calculated band structure and the effect of strain on hopping terms (Table S2). The band structure of GdSb resulting from our TB parametrization is presented in Figure 4(d) and Figure S2 over narrow and wide energy ranges, respectively. From Figure 4(a), it is apparent that the out-of-plane electron pocket centered at $Z$ is mainly composed of Gd $d_{xy}$ orbitals, which form $dd\sigma$-like bonds in the <110> direction and $dd\pi$-like bonds along the <101> direction (highlighted in Figure 4(b), with $dd\delta$ hopping being negligible, i.e., close to 0). The heavy- ($\delta$) and light- ($\beta$) hole bands are composed of Sb $p_x + p_y$ orbitals along $\Gamma - Z$, forming three different hopping terms $t_{1,2} = pp\pi \pm pp\sigma$ $t_3 = pp\pi$, and the split-off valence band ($\gamma$) is composed of $p_z$ orbitals. Moreover, $p$-$d$ mixing in GdSb through $pd\sigma$ and $pd\pi$ bond formation is necessary to describe the sharp conduction and valence band dispersions along $Z - W$. Similarly, the in-plane electron pockets at $X_1/X_2$ and $\delta$ hole band
dispersing along the $\Gamma - X_{1,2}$ axis are composed of Gd $d_{yz} / d_{xz}$ orbitals and Sb $p_y + p_z / p_x + p_z$ orbitals, respectively.

Upon applying compressive strain, the orbital overlap increases between the in-plane hopping terms of the $p_x p_y d_{xy}$ orbitals, leading to increased dispersion in both the valence and the conduction bands. However, because the $d$ orbital hopping terms have a stronger distance dependence than the $p$ orbitals (Figure 4(c))\textsuperscript{50}, the electron pocket has a more significant increase in its bandwidth moving from tensile to compressive strain. This behavior also explains the topological phase transition trend observed for RE-Vs due to lanthanide contraction\textsuperscript{16,22}. Lighter lanthanide elements have both larger ionic radius\textsuperscript{51} and larger unit cells\textsuperscript{52}, yet overall the ratio of the lanthanide ionic radius to the RE-V unit cell increases for the lighter lanthanides, leading to higher $d$-$d$ orbital overlap eventually resulting in band inversion, despite the decrease in $p$-$p$ orbital overlap.

The same response to strain (i.e., band inversion) predicted from the first-principles calculations along $\Gamma - Z$ in Figure 2(h) is reproduced in the TB model in Figure 4(d) and explains the more substantial modifications observed in ARPES and measured in DFT for band dispersions composed of atomic orbitals distributing within the film plane. For the in-plane electron pockets at $X_{1,2}$ under compressive strain, the $d$-$d$ orbital overlap in the $(011)/(101)$ faces is affected by both the reduced distance along $<010>/<100>$ and slightly expanded out-of-plane lattice parameter along $<001>$. However, due to the small Poisson ratio, the total distance between the $d_{xz}/d_{yz}$ orbitals decreases, leading to a slight reduction of the gap at the $X_{1,2}$. In conclusion, the TB model demonstrates the importance of both Gd-Gd $dd\sigma$ and Sb-Sb $pp\pi$ bonding in determining the degree of band inversion at the $Z$ high-symmetry point.

Finally, we address the effect of strain on the magnetic properties of GdSb. Due to the absence of orbital angular momentum in the $4f^7$ configuration of the Gd$^{3+}$ ion, GdSb represents an ideal isotropic Heisenberg model system for studying magnetic exchange interactions. GdSb can be considered a parent
compound of the half-Heusler structure GdPtV (V = Bi, Sb), which shows complex behavior such as an antiferromagnetic to ferromagnetic transition in GdPtSb due to strain-gradients\(^5\) and chiral anomaly and anisotropic magnetotransport in the predicted Weyl semimetal GdPtBi\(^{53}\). A 2.6 °C increase in the Néel temperature \((T_N)\) from +2% tensile (24.3 K) to −2% compressive (26.9 K) strained films is observed in Figure S3. Based on our TB model, a reduction in the lattice parameter results in increased \(p-d\) orbital hopping, which in turn leads to a higher \(T_N\) (see further details in Supporting Information). To our knowledge, this is the first study showing the direct impact of epitaxial strain on superexchange \(p-d\) hopping in a RE-V, but it also could guide future efforts in strain tuning the magnetic ordering temperature of additional materials beyond the RE-Vs family. Building on these results, the effect of strain/pressure in other RE-Vs with more complex magnetic behavior, such as Ce-V\(^{54}\) and Eu-VI\(^{55}\), can be modeled or applied for semiconducting RE-V nitrides such as ScN\(^{56}\) and GdN\(^{42}\).

In summary, we have followed with ARPES and DFT the evolution of the bulk band structure in biaxial strained GdSb quantum wells and demonstrated the tuning band topology in RE-Vs through epitaxial strain. We report the successful growth of strained GdSb films integrated with a conventional III-V semiconducting substrate, and resulting trends in magnetic ordering temperature and charge carrier ratios are discussed. The synthesis of high-quality epitaxial GdSb is an important step toward practical control of transport characteristics in magnetic Weyl semimetals. Our TB model based on nearest and next-nearest neighbor interactions describes well the electronic structure of GdSb. We have shown that biaxial compressive strain is expected to promote \(d-d\) hopping in the rare earth \(t_{2g}\) conduction bands to a larger extent than the pnictogen \(p\) band hopping, resulting in band inversion and a higher electron carrier density. This work opens the door to future studies of strain-controlled topological phase transitions and semimetal-semiconductor transitions in RE-Vs and RE-V derived compounds such as topological half-Heusler alloys (RE Pt/Pd V)\(^{57-59}\).
ASSOCIATED CONTENT

Supporting Information:

Additional details on ARPES surface preparation, DFT calculations, ARPES- and DFT-extracted Fermi wave vectors and band extrema, confinement effects, tight binding model construction, and magnetic properties of strained GdSb films.

AUTHOR INFORMATION

Corresponding Authors:

* Email: hadass@ucsb.edu (H.S.I.), cjpalm@ucsb.edu (C.J.P.)

ORCID

Hadass S. Inbar: https://orcid.org/0000-0002-8914-1162
Dai Q. Ho: https://orcid.org/0000-0002-3282-5862
Shouvik Chatterjee: https://orcid.org/0000-0002-8981-788X
Mihir Pendharkar: https://orcid.org/0000-0003-1857-6131
Aaron N. Engel: https://orcid.org/0000-0001-6687-4104
Shoaib Khalid: https://orcid.org/0000-0003-3806-3827
Yu Hao Chang: https://orcid.org/0000-0003-4098-7287
Shinichi Nishihaya: https://orcid.org/0000-0001-8320-1817
Alexei V. Fedorov: https://orcid.org/0000-0003-3510-3117
Donghui Lu: https://orcid.org/0000-0002-9708-0443
Makoto Hashimoto: https://orcid.org/0000-0003-1689-8997
Dan Read: https://orcid.org/0000-0002-4178-4986
Anderson Janotti: https://orcid.org/0000-0002-0358-2101
Christopher J. Palmstrøm: https://orcid.org/0000-0003-4884-4512
Present Addresses

# Department of Condensed Matter Physics and Materials Science, Tata Institute of Fundamental Research, Mumbai 400005, India

† Department of Physics, School of Natural Sciences, National University of Science and Technology, Islamabad 44000, Pakistan

♦ Department of Materials Science and Engineering, Stanford University, Stanford, CA, 94305 USA.

‡ Department of Physics, Tokyo Institute of Technology, Tokyo, 152-8551, Japan

AUTHOR CONTRIBUTIONS:

H.S.I. and C.J.P. conceived the study. Thin film growth, x-ray diffraction, and transport measurements were performed by H.S.I. with assistance from S.C., C.P.D., and M.P. ARPES measurements were performed by H.S.I. with assistance from S.C., A.N.E., Y.C. S.N., D.R., A.V.F., D.L., M.H. and analyzed by H.S.I. DFT calculations were performed by D.Q.H. with assistance from S.K., and A.J. supervising. H.S.I. and D.Q.H. constructed the tight-binding model. S.C., A.N.E., C.P.D., M.P. and designed ultra-high vacuum components and sample holders. The manuscript was prepared by H.S.I., D.Q.H., A.J., and C.J.P. All authors discussed the results and commented on the manuscript.

ACKNOWLEDGMENTS:

Synthesis of thin films, development of a prototype ultra-high vacuum suitcase, ARPES experiments, and theoretical work were supported by the U.S. Department of Energy (contract no. DE-SC0014388). Development of the growth facilities and low-temperature magnetotransport measurements were supported by the Office of Naval Research through the Vannevar Bush Faculty Fellowship under award no. N00014-15-1-2845. Scanning probe studies were supported by NSF (award number DMR-
1507875). This research used resources of the Advanced Light Source, which is a DOE Office of Science User Facility under contract no. DE-AC02-05CH11231. Use of the Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratory, is supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Contract No. DE-AC02-76SF00515. We acknowledge the use of shared facilities of the NSF Materials Research Science and Engineering Center (MRSEC) at the University of California Santa Barbara (DMR 1720256). DFT calculations used the National Energy Research Scientific Computing Center (NERSC), a U.S. Department of Energy Office of Science User Facility operated under contract no. DE-AC02-05CH11231. H. S. I. gratefully acknowledges support from the UC Santa Barbara NSF Quantum Foundry funded via the Q-AMASE-i program under award DMR-1906325 and support for further developments of the vacuum suitcases. D.Q.H. acknowledges support from NSF through the University of Delaware Materials Research Science and Engineering Center, DMR-2011824.
FIGURES:

**Figure 1.** (a) Crystal structure and epitaxial relationship of the rock salt GdSb / zinc-blende III-V (001) orientation. Reciprocal space maps of the (226) reflection in (b) −2% compressive and (c) +2% tensile strained GdSb films, demonstrating coherent growth to the underlying III-V layer. (c) Biaxial strain window of GdSb and range of III-V band gaps and lattice parameters used for the buffer layer growth. (d) Scanning tunneling microscope image of the −2% compressive strained film: 4 nm GdSb / GaSb (001) (V = −0.5 V, I=1 nA).
Figure 2. Band dispersion of the electron pockets and hole bands in GdSb films studied with ARPES and strain-induced modifications for +2% tensile (left) and −2% compressive (right) biaxial strain. (a), (c), and (e) Schematics of the bulk Brillouin zone projected to the (001) surface Brillouin zone, showing the measured $k_z$ plane (pink square) and $E$-$k$ spectra directions (black line). $\bar{\Gamma} - \bar{M} - \bar{\Gamma}$ cut along the in-plane electron pockets $X_{1,2}$ for the (a,b) semimajor axis ($\bar{\Gamma} - X_1 - \bar{\Gamma}$) measured at $k_z=Z$ with a photon energy of 94 eV, and (c,d) semiminor axis ($W - X_2 - W$) measured at $k_z=\Gamma$ with a photon energy of 60 eV. (e,f) $\bar{M} - \bar{\Gamma} - \bar{M}$ cuts of the out-of-plane electron pocket semiminor axis ($W - Z - W$) measured at $k_z=Z$ with a photon energy of 88 eV. Black dotted lines are hyperbolic fits to the band dispersions and the green dotted lines highlight the band shifts. Fermi wave vectors and band extrema extracted from the fits are detailed in Table S1. (g-h) HSE06-calculated band structures for $\varepsilon = +2, -2\%$ along (g) the in-plane high-symmetry points and (h) film plane normal direction. Fermi levels were set at 0. Shaded regions highlight the $E$-$k$ cuts in panels (b,d,f).
Figure 3. $E$-$k$ dispersion of the hole pockets in the biaxial strained GdSb films measured at $k_z = \Gamma$ (photon energy of 60 eV). ARPES spectra near the Fermi level highlighting the same $\gamma$ band position and overlaid fits along (a,b) $\overline{M} - \overline{\Gamma} - \overline{M}$ and (c,d) $\overline{X} - \overline{\Gamma} - \overline{X}$. Top panel: raw data, bottom panel curvature plot of the raw data. (e-h) Wider energy range of the same cuts in (a-d), showing the quantum well states. The plots on the right side present the raw data, and the left side shows the curvature plot. Fermi wave vectors extracted from the fits to the valence band and band extrema in panels (e-h) are detailed in Table S1.
Figure 4. Strain effect on orbital overlap in GdSb. (a) nonmagnetic DFT HSE calculations of the electronic band structure in GdSb and the orbital character of the DFT wavefunctions. (b) Illustration of relevant atomic orbitals and primary interaction paths at the Z point. (C) Tight binding hopping term decay rate with increasing strain (Supporting Information for details) and the evolution of the calculated gap at the TRIM Z point vs strain. (d) Tight binding band structure of GdSb and dependence on the strain level.
REFERENCES:

(1) Kim, J. M.; Haque, M. F.; Hsieh, E. Y.; Nahid, S. M.; Zarin, I.; Jeong, K.; So, J.; Park, H.; Nam, S. Strain Engineering of Low-Dimensional Materials for Emerging Quantum Phenomena and Functionalities. *Adv. Mater.* **2022**, *2107362*, 2107362. https://doi.org/10.1002/adma.202107362.

(2) Leubner, P.; Lunczer, L.; Brüne, C.; Buhmann, H.; Molenkamp, L. W. Strain Engineering of the Band Gap of HgTe Quantum Wells Using Superlattice Virtual Substrates. *Phys. Rev. Lett.* **2016**, *117* (8), 086403. https://doi.org/10.1103/PhysRevLett.117.086403.

(3) Walkup, D.; Assaf, B. A.; Scipioni, K. L.; Sankar, R.; Chou, F.; Chang, G.; Lin, H.; Zeljkovic, I.; Madhavan, V. Interplay of Orbital Effects and Nanoscale Strain in Topological Crystalline Insulators. *Nat. Commun.* **2018**, *9* (1), 1550. https://doi.org/10.1038/s41467-018-03887-5.

(4) Nayak, A. K.; Reiner, J.; Queiroz, R.; Fu, H.; Shekhar, C.; Yan, B.; Felser, C.; Avraham, N.; Beidenkopf, H. Resolving the Topological Classification of Bismuth with Topological Defects. *Sci. Adv.* **2019**, *5* (11), 37–42. https://doi.org/10.1126/sciadv.aax6996.

(5) Du, D.; Manzo, S.; Zhang, C.; Saraswat, V.; Genser, K. T.; Rabe, K. M.; Voyles, P. M.; Arnold, M. S.; Kawasaki, J. K. Epitaxy, Exfoliation, and Strain-Induced Magnetism in Rippled Heusler Membranes. *Nat. Commun.* **2021**, *12* (1), 2494. https://doi.org/10.1038/s41467-021-22784-y.

(6) Barfuss, A.; Dudy, L.; Scholz, M. R.; Roth, H.; Höpfner, P.; Blumenstein, C.; Landolt, G.; Dil, J. H.; Plumb, N. C.; Radovic, M.; Bostwick, A.; Rotenberg, E.; Fleszar, A.; Bihlmayer, G.; Wortmann, D.; Li, G.; Hanke, W.; Claessen, R.; Schäfer, J. Elemental Topological Insulator with Tunable Fermi Level: Strained Alpha-Sn on InSb(001). *Phys. Rev. Lett.* **2013**, *111* (15), 157205.
Phan, G. N.; Nakayama, K.; Sugawara, K.; Sato, T.; Urata, T.; Tanabe, Y.; Tanigaki, K.; Nabeshima, F.; Imai, Y.; Maeda, A.; Takahashi, T. Effects of Strain on the Electronic Structure, Superconductivity, and Nematicity in FeSe Studied by Angle-Resolved Photoemission Spectroscopy. *Phys. Rev. B* 2017, 95 (22), 1–6. https://doi.org/10.1103/PhysRevB.95.224507.

Walsh, L. A.; Hinkle, C. L. Van Der Waals Epitaxy: 2D Materials and Topological Insulators. *Appl. Mater. Today* 2017, 9, 504–515. https://doi.org/10.1016/j.apmt.2017.09.010.

Brahlek, M.; Lapano, J.; Lee, J. S. Topological Materials by Molecular Beam Epitaxy. *J. Appl. Phys.* 2020, 128 (21), 210902. https://doi.org/10.1063/5.0022948.

Flötotto, D.; Bai, Y.; Chan, Y. H.; Chen, P.; Wang, X.; Rossi, P.; Xu, C. Z.; Zhang, C.; Hlevyack, J. A.; Denlinger, J. D.; Hong, H.; Chou, M. Y.; Mittemeijer, E. J.; Eckstein, J. N.; Chiang, T. C. In Situ Strain Tuning of the Dirac Surface States in Bi2Se3 Films. *Nano Lett.* 2018, 18 (9), 5628–5632. https://doi.org/10.1021/acs.nanolett.8b02105.

Riccò, S.; Kim, M.; Tamai, A.; McKeown Walker, S.; Bruno, F. Y.; Cucchi, I.; Cappelli, E.; Besnard, C.; Kim, T. K.; Dudin, P.; Hoesch, M.; Gutmann, M. J.; Georges, A.; Perry, R. S.; Baumberger, F. In Situ Strain Tuning of the Metal-Insulator-Transition of Ca2RuO4 in Angle-Resolved Photoemission Experiments. *Nat. Commun.* 2018, 9 (1), 4535. https://doi.org/10.1038/s41467-018-06945-0.

Sunko, V.; Abarca Morales, E.; Marković, I.; Barber, M. E.; Milosavljević, D.; Mazzola, F.; Sokolov, D. A.; Kikugawa, N.; Cacho, C.; Dudin, P.; Rosner, H.; Hicks, C. W.; King, P. D. C.; Mackenzie, A. P. Direct Observation of a Uniaxial Stress-Driven Lifshitz Transition in Sr2RuO4.
(13) Lin, C.; Ochi, M.; Noguchi, R.; Kuroda, K.; Sakoda, M.; Nomura, A.; Tsubota, M.; Zhang, P.; Bareille, C.; Kurokawa, K.; Arai, Y.; Kawaguchi, K.; Tanaka, H.; Yaji, K.; Harasawa, A.; Hashimoto, M.; Lu, D.; Shin, S.; Arita, R.; Tanda, S.; Kondo, T. Visualization of the Strain-Induced Topological Phase Transition in a Quasi-One-Dimensional Superconductor TaSe3. Nat. Mater. 2021, 20 (8), 1093–1099. https://doi.org/10.1038/s41535-019-0185-9.

(14) Burganov, B.; Adamo, C.; Mulder, A.; Uchida, M.; King, P. D. C.; Harter, J. W.; Shai, D. E.; Gibbs, A. S.; Mackenzie, A. P.; Uecker, R.; Bruetzam, M.; Beasley, M. R.; Fennie, C. J.; Schlom, D. G.; Shen, K. M. Strain Control of Fermiology and Many-Body Interactions in Two-Dimensional Ruthenates. Phys. Rev. Lett. 2016, 116 (19), 197003. https://doi.org/10.1103/PhysRevLett.116.197003.

(15) Ruf, J. P.; Paik, H.; Schreiber, N. J.; Nair, H. P.; Miao, L.; Kawasaki, J. K.; Nelson, J. N.; Faeth, B. D.; Lee, Y.; Goodge, B. H.; Pamuk, B.; Fennie, C. J.; Kourkoutis, L. F.; Schlom, D. G.; Shen, K. M. Strain-Stabilized Superconductivity. Nat. Commun. 2021, 12 (1), 59. https://doi.org/10.1038/s41467-020-20252-7.

(16) Duan, X.; Wu, F.; Chen, J.; Zhang, P.; Liu, Y.; Yuan, H.; Cao, C. Tunable Electronic Structure and Topological Properties of LnPn (Ln=Ce, Pr, Sm, Gd, Yb; Pn=Sb, Bi). Commun. Phys. 2018, 1 (1), 71. https://doi.org/10.1038/s42005-018-0074-8.

(17) Tafti, F. F.; Torikachvili, M. S.; Stillwell, R. L.; Baer, B.; Stavrou, E.; Weir, S. T.; Vohra, Y. K.; Yang, H.-Y.; McDonnell, E. F.; Kushwaha, S. K.; Gibson, Q. D.; Cava, R. J.; Jeffries, J. R. Tuning the Electronic and the Crystalline Structure of LaBi by Pressure: From Extreme Magnetoresistance to Superconductivity. Phys. Rev. B 2017, 95 (1), 014507.
(18) Xu, C. Q.; Li, B.; van Delft, M. R.; Jiao, W. H.; Zhou, W.; Qian, B.; Zhigadlo, N. D.; Qian, D.; Sankar, R.; Hussey, N. E.; Xu, X. Extreme Magnetoresistance and Pressure-Induced Superconductivity in the Topological Semimetal Candidate YBi. Phys. Rev. B 2019, 99 (2), 024110. https://doi.org/10.1103/PhysRevB.99.024110.

(19) Zhang, M.; Wang, X.; Rahman, A.; Dai, R.; Wang, Z.; Zhang, Z. Observation of Superconductivity Accompanying the Pressure-Induced Structural Phase Transition in LaSb. Phys. Rev. B 2020, 101 (6), 064106. https://doi.org/10.1103/PhysRevB.101.064106.

(20) Inoue, H.; Han, M.; Hu, M.; Suzuki, T.; Liu, J.; Checkelsky, J. G. Band Engineering of a Magnetic Thin Film Rare-Earth Monopnictide: A Platform for High Chern Number. Phys. Rev. Mater. 2019, 3 (10), 101202. https://doi.org/10.1103/PhysRevMaterials.3.101202.

(21) Khalid, S.; Sabino, F. P.; Janotti, A. Topological Phase Transition in LaAs under Pressure. Phys. Rev. B 2018, 98 (22), 220102. https://doi.org/10.1103/PhysRevB.98.220102.

(22) Li, P.; Wu, Z.; Wu, F.; Cao, C.; Guo, C.; Wu, Y.; Liu, Y.; Sun, Z.; Cheng, C.-M.; Lin, D.-S.; Steglich, F.; Yuan, H.; Chiang, T.-C.; Liu, Y. Tunable Electronic Structure and Surface States in Rare-Earth Monobismuthides with Partially Filled f Shell. Phys. Rev. B 2018, 98 (8), 085103. https://doi.org/10.1103/PhysRevB.98.085103.

(23) Kim, J.; Kim, H.-S.; Vanderbilt, D. Nearly Triple Nodal Point Topological Phase in Half-Metallic GdN. Phys. Rev. B 2018, 98 (15), 155122. https://doi.org/10.1103/PhysRevB.98.155122.

(24) Inbar, H. S.; Ho, D. Q.; Chatterjee, S.; Pendharkar, M.; Engel, A. N.; Dong, J. T.; Khalid, S.; Chang, Y. H.; Guo, T.; Fedorov, A. V.; Lu, D.; Hashimoto, M.; Read, D.; Janotti, A.; Palmstrøm, C. J.
Epitaxial Growth, Magnetoresistance, and Electronic Band Structure of GdSb Magnetic Semimetal Films. 2022.

(25) Li, D. X.; Haga, Y.; Shida, H.; Suzuki, T.; Kwon, Y. S.; Kido, G. Magnetic Properties of Stoichiometric Gd Monopnictides. *J. Phys. Condens. Matter* **1997**, *9* (48), 10777–10788. https://doi.org/10.1088/0953-8984/9/48/019.

(26) Palmstrøm, C. J. Epitaxy of Dissimilar Materials. *Annu. Rev. Mater. Sci.* **1995**, *25* (1), 389–415. https://doi.org/10.1146/annurev.ms.25.080195.002133.

(27) Bomberger, C. C.; Lewis, M. R.; Vanderhoef, L. R.; Doty, M. F.; Zide, J. M. O. Review Article: Overview of Lanthanide Pnictide Films and Nanoparticles Epitaxially Incorporated into III-V Semiconductors. *J. Vac. Sci. Technol. B* **2017**, *35* (3), 030801. https://doi.org/10.1116/1.4979347.

(28) Sands, T.; Palmstrøm, C. J.; Harbison, J. P.; Keramidas, V. G.; Tabatabaie, N.; Cheeks, T. L.; Ramesh, R.; Silberberg, Y. Stable and Epitaxial Metal/III-V Semiconductor Heterostructures. *Mater. Sci. Reports* **1990**, *5* (3), 99–170. https://doi.org/10.1016/S0920-2307(05)80003-9.

(29) Kadow, C.; Fleischer, S. B.; Ibbetson, J. P.; Bowers, J. E.; Gossard, A. C.; Dong, J. W.; Palmstrøm, C. J. Self-Assembled ErAs Islands in GaAs: Growth and Subpicosecond Carrier Dynamics. *Appl. Phys. Lett.* **1999**, *75* (22), 3548–3550. https://doi.org/10.1063/1.125384.

(30) O’Hara, J. F.; Zide, J. M. O.; Gossard, A. C.; Taylor, A. J.; Averitt, R. D. Enhanced Terahertz Detection via ErAs:GaAs Nanoisland Superlattices. *Appl. Phys. Lett.* **2006**, *88* (25), 251119. https://doi.org/10.1063/1.2216026.

(31) Kim, W.; Zide, J.; Gossard, A.; Klenov, D.; Stemmer, S.; Shakouri, A.; Majumdar, A. Thermal Conductivity Reduction and Thermoelectric Figure of Merit Increase by Embedding Nanoparticles
in Crystalline Semiconductors. Phys. Rev. Lett. **2006**, *96* (4), 045901. https://doi.org/10.1103/PhysRevLett.96.045901.

(32) Lu, H.; Burke, P. G.; Gossard, A. C.; Zeng, G.; Ramu, A. T.; Bahk, J.-H.; Bowers, J. E. Semimetal/Semiconductor Nanocomposites for Thermoelectrics. *Adv. Mater.* **2011**, *23* (20), 2377–2383. https://doi.org/10.1002/adma.201100449.

(33) Krivoy, E. M.; Vasudev, A. P.; Rahimi, S.; Synowicki, R. A.; McNicholas, K. M.; Ironside, D. J.; Salas, R.; Kelp, G.; Jung, D.; Nair, H. P.; Shvets, G.; Akinwande, D.; Lee, M. L.; Brongersma, M. L.; Bank, S. R. Rare-Earth Monopnictide Alloys for Tunable, Epitaxial, Designer Plasmonics. *ACS Photonics* **2018**, *5* (8), 3051–3056. https://doi.org/10.1021/acsphotonics.8b00288.

(34) Schultz, B. D.; Farrell, H. H.; Evans, M. M. R.; Lüdge, K.; Palmstrøm, C. J. ErAs Interlayers for Limiting Interfacial Reactions in Fe/GaAs(100) Heterostructures. *J. Vac. Sci. Technol. B Microelectron. Nanom. Struct.* **2002**, *20* (4), 1600. https://doi.org/10.1116/1.1491994.

(35) Heyd, J.; Scuseria, G. E.; Ernzerhof, M. Hybrid Functionals Based on a Screened Coulomb Potential. *J. Chem. Phys.* **2003**, *118* (18), 8207–8215. https://doi.org/10.1063/1.1564060.

(36) Heyd, J.; Scuseria, G. E.; Ernzerhof, M. Erratum: “Hybrid Functionals Based on a Screened Coulomb Potential” [J. Chem. Phys. 118, 8207 (2003)]. *J. Chem. Phys.* **2006**, *124* (21), 219906. https://doi.org/10.1063/1.2204597.

(37) Kresse, G.; Hafner, J. Ab Initio Molecular Dynamics for Liquid Metals. *Phys. Rev. B* **1993**, *47* (1), 558–561. https://doi.org/10.1103/PhysRevB.47.558.

(38) Kresse, G.; Hafner, J. Ab Initio Molecular-Dynamics Simulation of the Liquid-Metal–Amorphous-Semiconductor Transition in Germanium. *Phys. Rev. B* **1994**, *49* (20), 14251–14269.
(39) Chatterjee, S.; Khalid, S.; Inbar, H. S.; Goswami, A.; Guo, T.; Chang, Y.-H.; Young, E.; Fedorov, A. V.; Read, D.; Janotti, A.; Palmstrøm, C. J. Controlling Magnetoresistance by Tuning Semimetallicity through Dimensional Confinement and Heteroepitaxy. *Sci. Adv.* **2021**, *7* (16), eabe8971. https://doi.org/10.1126/sciadv.abe8971.

(40) York, B. R. Residual Stress/Strain Analysis in Thin Films by X-Ray Diffraction. *Crit. Rev. Solid State Mater. Sci.* **1995**, *20* (2), 125–177. https://doi.org/10.1080/10408439508243733.

(41) Mir, S. H.; Jha, P. C.; Islam, M. S.; Banerjee, A.; Luo, W.; Dabhi, S. D.; Jha, P. K.; Ahuja, R. Static and Dynamical Properties of Heavy Actinide Monopnictides of Lutetium. *Sci. Rep.* **2016**, *6* (1), 29309. https://doi.org/10.1038/srep29309.

(42) Duan, C.; Sabiryanov, R. F.; Liu, J.; Mei, W. N.; Dowben, P. A.; Hardy, J. R. Strain Induced Half-Metal to Semiconductor Transition in GdN. *Phys. Rev. Lett.* **2005**, *94* (23), 237201. https://doi.org/10.1103/PhysRevLett.94.237201.

(43) Kuroda, K.; Ochi, M.; Suzuki, H. S.; Hirayama, M.; Nakayama, M.; Noguchi, R.; Bareille, C.; Akebi, S.; Kunisada, S.; Muro, T.; Watson, M. D.; Kitazawa, H.; Haga, Y.; Kim, T. K.; Hoesch, M.; Shin, S.; Arita, R.; Kondo, T. Experimental Determination of the Topological Phase Diagram in Cerium Monopnictides. *Phys. Rev. Lett.* **2018**, *120* (8), 086402. https://doi.org/10.1103/PhysRevLett.120.086402.

(44) Nummy, T. J.; Waugh, J. A.; Parham, S. P.; Liu, Q.; Yang, H.-Y.; Li, H.; Zhou, X.; Plumb, N. C.; Tafti, F. F.; Dessau, D. S. Measurement of the Atomic Orbital Composition of the Near-Fermi-Level Electronic States in the Lanthanum Monopnictides LaBi, LaSb, and LaAs. *npj Quantum
Observation of Topological Surface States and Strong Electron/Hole Imbalance in Extreme Magnetoresistance Compound LaBi. *Phys. Rev. Mater.* **2018**, *2* (2), 024201. https://doi.org/10.1103/PhysRevMaterials.2.024201.

Khalid, S.; Janotti, A. Trivial to Nontrivial Topology Transition in Rare-Earth Pnictides with Epitaxial Strain. *Phys. Rev. B* **2020**, *102* (3), 035151. https://doi.org/10.1103/PhysRevB.102.035151.

Fu, L.; Kane, C. L. Topological Insulators with Inversion Symmetry. *Phys. Rev. B* **2007**, *76* (4), 045302. https://doi.org/10.1103/PhysRevB.76.045302.

Mong, R. S. K.; Essin, A. M.; Moore, J. E. Antiferromagnetic Topological Insulators. *Phys. Rev. B* **2010**, *81* (24), 245209. https://doi.org/10.1103/PhysRevB.81.245209.

Sun, Y.; Thompson, S. E.; Nishida, T. Physics of Strain Effects in Semiconductors and Metal-Oxide-Semiconductor Field-Effect Transistors. *J. Appl. Phys.* **2007**, *101* (10), 104503. https://doi.org/10.1063/1.2730561.

Harrison, W. A. *Electronic Structure and the Properties of Solids: The Physics of the Chemical Bond*; Dover Publications, 2012.

Jia, Y. Q. Crystal Radii and Effective Ionic Radii of the Rare Earth Ions. *J. Solid State Chem.* **1991**, *95* (1), 184–187. https://doi.org/10.1016/0022-4596(91)90388-X.

Abdusalyamova, M. N.; Shokirov, H. S.; Rakhmatov, O. I. Investigation of the Rare Earth
Monoantimonides. *J. Less Common Met.* **1990**, *166* (2), 221–227. https://doi.org/10.1016/0022-5088(90)90003-3.

(53) Schindler, C.; Galeski, S.; Schnelle, W.; Wawrzyńczak, R.; Abdel-Haq, W.; Guin, S. N.; Kroder, J.; Kumar, N.; Fu, C.; Borrmann, H.; Shekhar, C.; Felser, C.; Meng, T.; Grushin, A. G.; Zhang, Y.; Sun, Y.; Gooth, J. Anisotropic Electrical and Thermal Magnetotransport in the Magnetic Semimetal GdPtBi. *Phys. Rev. B* **2020**, *101* (12), 125119. https://doi.org/10.1103/PhysRevB.101.125119.

(54) Jang, S.; Kealhofer, R.; John, C.; Doyle, S.; Hong, J.; Shim, J. H.; Si, Q.; Erten, O.; Denlinger, J. D.; Analytis, J. G. Direct Visualization of Coexisting Channels of Interaction in CeSb. *Sci. Adv.* **2019**, *5* (3), eaat7158. https://doi.org/10.1126/sciadv.aaat7158.

(55) Kępa, H.; Springholz, G.; Giebultowicz, T. M.; Goldman, K. I.; Majkrzak, C. F.; Kaacman, P.; Blinowski, J.; Holl, S.; Krenn, H.; Bauer, G. Magnetic Interactions in EuTe Epitaxial Layers and EuTe/PbTe Superlattices. *Phys. Rev. B* **2003**, *68* (2), 024419. https://doi.org/10.1103/PhysRevB.68.024419.

(56) Biswas, B.; Saha, B. Development of Semiconducting ScN. *Phys. Rev. Mater.* **2019**, *3* (2), 020301. https://doi.org/10.1103/PhysRevMaterials.3.020301.

(57) Al-Sawai, W.; Lin, H.; Markiewicz, R. S.; Wray, L. A.; Xia, Y.; Xu, S.-Y.; Hasan, M. Z.; Bansil, A. Topological Electronic Structure in Half-Heusler Topological Insulators. *Phys. Rev. B* **2010**, *82* (12), 125208. https://doi.org/10.1103/PhysRevB.82.125208.

(58) Chadov, S.; Qi, X.; Kübler, J.; Fecher, G. H.; Felser, C.; Zhang, S. C. Tunable Multifunctional Topological Insulators in Ternary Heusler Compounds. *Nat. Mater.* **2010**, *9* (7), 541–545. https://doi.org/10.1038/nmat2770.
Lin, H.; Wray, L. A.; Xia, Y.; Xu, S.; Jia, S.; Cava, R. J.; Bansil, A.; Hasan, M. Z. Half-Heusler Ternary Compounds as New Multifunctional Experimental Platforms for Topological Quantum Phenomena. *Nat. Mater.* **2010**, *9* (7), 546–549. https://doi.org/10.1038/nmat2771.
Strain Tuning the Band Topology of Epitaxial GdSb Quantum Wells:

Supporting Information

Hadass S. Inbar1*, Dai Q. Ho2,3*, Shouvik Chatterjee4#, Aaron N. Engel1, Shoaib Khalid2†, Connor P. Dempsey4, Mihir Pendharkar4*, Yu Hao Chang1, Shinichi Nishihaya1‡, Alexei V. Fedorov5, Donghui Lu6, Makoto Hashimoto6, Dan Read4,7, Anderson Janotti2, Christopher J. Palmstrøm1,4*

1Materials Department, University of California Santa Barbara, Santa Barbara, CA 93106, USA
2Department of Materials Science and Engineering, University of Delaware, Newark, DE 19716, USA
3Faculty of Natural Sciences, Quy Nhon University, Quy Nhon 59000, Vietnam
4Electrical and Computer Engineering Department, University of California Santa Barbara, Santa Barbara, CA 93106, USA
5Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA
6Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratory, CA, USA
7School of Physics and Astronomy, Cardiff University, Cardiff CF24 3AA, UK
*These authors contributed equally

* Email: hadass@ucsb.edu (H.S.I.), ejpalm@ucsb.edu (C.J.P.)

(Dated: November 27, 2022)

Present Addresses

# Department of Condensed Matter Physics and Materials Science, Tata Institute of Fundamental Research, Mumbai 400005, India
† Department of Physics, School of Natural Sciences, National University of Science and Technology, Islamabad 44000, Pakistan
*Department of Materials Science and Engineering, Stanford University, Stanford, CA, 94305 USA.
‡ Department of of Physics, Tokyo Institute of Technology, Tokyo, 152-8551, Japan
I. Supp. Info I  

ARPES surface preparation  

ARPES measurements at the Advanced Light Source (ALS) were conducted at 11 K and at the Stanford Synchrotron Radiation Lightsource (SSRL) at 20 K. Both were acquired with a Scienta DA30L hemispherical analyzer with a total energy resolution better than 20 meV. ALS measurements were conducted for \textit{in vacuo} transferred samples, where a custom-built vacuum suitcase with a base pressure <10^{-10} \text{Torr was used to transfer films from the growth chamber at UC, Santa Barbara, to beamline 10.0.1.2 at the ALS in Berkeley. The SSRL measurements at beamline 5−2 were performed for \textit{ex situ} transferred films. To prevent oxidation of the GdSb films during the \textit{ex situ} transfer to SSRL, a thick \textasciitilde 800 nm antimony capping layer was deposited with Sb\textsubscript{2} flux after GdSb growth during sample cool down beginning at a temperature of 230-130 \textdegree C. Before measurement, samples were heated to 420 ± 20 \textdegree C (calibrated by pyrometry) in an ultra-high vacuum chamber and held at that temperature for \textasciitilde 30 min to fully desorb the Sb cap. The potential thermal decomposition of the In\textsubscript{x}Ga\textsubscript{1-x}Sb buffer film limits the maximum annealing temperature. During the final stage of Sb desorption, a spike in pressure to 1e-8 Torr was observed, and the film surface visually transitioned from a shiny to a hazy-matt finish and back to a polished appearance. The thermal desorption window of the Sb cap was confirmed by scanning tunneling microscopy at UCSB and at the SSRL beamline by examination of the Sb 4d and Gd f core levels. All films showed no evidence of oxidation in XPS scans: a single binding energy component in the Gd 4f level was seen, and no Oxygen 2s core levels were present. An Sb-related surface state was observed for all films and was remarkably stable for the compressive film, see sharp linear dispersions crossing the Fermi level at $k_F \sim 0.9$ Å$^{-1}$ in Figure 2(d). The Fermi surface of the surface state differs from the expected electronic band structure of elemental Sb and might have originated from a stabilized square-net Sb-rich surface reconstruction\textsuperscript{1}.  

2
DFT calculations

The Gd $4f$ electrons were treated as valence electrons for antiferromagnet (AFM) calculations in Figure 2(g-h), whereas for the nonmagnetic phase calculation in Figure S1 the $4f$ electrons were treated as core electrons. The configurations of valence shells of Gd and Sb are $4f^75s^25p^65d^{10}6s^1$ and $5s^25p^3$, respectively. We used the calculated equilibrium lattice parameter of 6.197 Å for GdSb to consistently determine the Poisson ratio. Kohn-Sham orbitals in DFT\textsuperscript{2,3} were expanded using a plane-wave basis set with the value of energy cutoff of 400 eV. Interactions between ion cores and valence electrons were described by the projector augmented wave (PAW) method\textsuperscript{4}. We used a rhombohedral unit cell consisting of 4 atoms for the magnetic phase calculations to simulate the AFM state in GdSb. The local magnetic moment on each Gd site was constrained to point along $[\bar{1}12]$ direction. An $8 \times 8 \times 8 \Gamma$-centered k-point mesh was used for integration over the first Brillouin zone. The folded band structure of the AFM unit cell was then unfolded back to the FCC primitive unit cell to facilitate a direct comparison with ARPES data\textsuperscript{5,6}.

The Fermi surface and Fermi volume were obtained by Wannier interpolation from first principles using the nonmagnetic phase. Since the Gd $d$ and Sb $p$ are relevant orbitals around the Fermi level, they were used as the starting projectors for the Wannier orbitals construction. The charge carrier concentrations were then estimated from obtained Fermi volumes by using the SKEAF code\textsuperscript{7}. Hopping term values used in constructing the TB model were extracted from the Wannier orbitals-based Hamiltonian, which is directly achieved from the wannierization process.

We have further investigated the consequence of the size quantization effect on the 4 nm thin films by performing the calculations for 4-nm-thick freestanding slabs in Figure S1. Unstrained and in-plane strained cases were simulated using a supercell consisting of 13 monolayers (ML, 2 ML in one unit cell) thick slabs along the [001] direction, assuming a nonmagnetic phase. A vacuum space of at
least 20 Å was included in the [001] direction of the supercell to remove the artificial interaction between images of the slabs.

ARPES- and DFT-extracted Fermi wave vectors and band extrema

Table S1 lists band positions collected via ARPES and results from DFT calculations. The values of hole and electron carrier Fermi wave vectors for both GdSb strain levels are similar to other bulk crystal RE-Vs compounds studied with ARPES\textsuperscript{8–13}. Comparison to other RE-Vs also demonstrates that for in-plane dispersions, biaxial lattice compression shows a similar trend as chemical pressure induced by lanthanide contraction; a smaller lattice parameter leads to a higher chemical potential\textsuperscript{13,14}. The experimental Fermi velocity of both the hole and electron carriers does not show a significant change as a function of strain, which can be explained by the relatively high energy separation of the Fermi level from the band extrema, where most effective mass changes are expected to take place\textsuperscript{15}. Along the semimajor axis in Figure 2(a-b), the Fermi wave vector increases with compressive strain, whereas it shows a smaller variation along the semi-minor axis (Figure 2(c-d)) for the in-plane pockets. In addition to modifying the band topology, the compressively strained film is more electron-rich and is further away from exact carrier compensation than the tensile strained film.

Table S1 also shows the compressive strained film DFT-calculated values after applying a rigid Fermi level shift. This could be required due to experimental modifications such as bulk doping or Fermi-level pinning. One source of surface Fermi level pinning could be the trivial surface states observed for the compressively strained film (see the earlier section on ARPES surface preparation). By shifting the Fermi level position upward in our DFT calculation by +0.15 eV in the −2\% strained film (so that both films have the same γ band maximum position) in Table S1, we obtain better agreement between the hole band Fermi wave vectors, yet a larger discrepancy between the experimental electron pocket values and hole band extrema at $X_{1,2}$. Therefore, alternative corrections to the modeled valence band are required to reach a better agreement with the ARPES results.
Table S1. Fermi surface of 4-nm-thick strained GdSb (001) films. Band maximum/minimum energy positions, Fermi wave vectors ($k_F$) for all bands, obtained from the ARPES measurements, and DFT calculations, and DFT calculations accounting for Fermi level pinning in the −2% compressively strained film

| $\alpha$ Band Extrema (eV) | $k_F$ (Å⁻¹) | Minor $W-X$ | Major $\Gamma-X$ | +2% (tensile strain) | −2% (compressive strain) |
|----------------------------|-------------|-------------|-------------------|---------------------|-------------------------|
|                            |             | $X_{1,2}$   | $Z$               | ARPES | DFT | ARPES | DFT | DFT+0.15eV |
|                            | $0.085 (±0.02)$ | 0.103       | 0.084 (±0.02)     | 0.110 | 0.134 |
|                            | $0.11 (±0.05)$ | 0.108       | 0.089 (±0.02)     | 0.103 | 0.128 |
|                            | $0.356 (±0.02)$ | 0.374       | 0.371 (±0.03)     | 0.423 | 0.482 |
|                            | NA          | 0.364       | NA                | 0.434 | 0.495 |

| $\alpha$ Band Extrema (eV) | $k_F$ (Å⁻¹) | Minor $W-X$ | Major $\Gamma-X$ | +2% (tensile strain) | −2% (compressive strain) |
|----------------------------|-------------|-------------|-------------------|---------------------|-------------------------|
|                            |             | $X_{1,2}$   | $Z$               | ARPES | DFT | ARPES | DFT | DFT+0.15eV |
|                            | $-0.375 (±0.004)$ | $-0.405$   | $-0.440 (±0.004)$ | $-0.540$ | $-0.690$ |
|                            | $-0.118 (±0.006)$ | $a_2$: $-0.157 (±0.004)$ | $-0.540$ | $-0.690$ |
|                            | NA          | NA          | NA                | NA                | NA                      |

| $\delta$ Band Extrema (eV) | $k_F$ (Å⁻¹) | $\bar{M} - \bar{\Gamma} - \bar{M}$ | $\bar{X} - \bar{\Gamma} - \bar{X}$ | +2% (tensile strain) | −2% (compressive strain) |
|----------------------------|-------------|------------------------------------|------------------------------------|---------------------|-------------------------|
|                            |             | $0.230 (±0.030)$ | $0.238$                           | $0.184 (±0.030)$     | $0.248$ | $0.202$ |
|                            |             | $0.123 (±0.01)$ | $0.175$                           | $0.124 (±0.018)$     | $0.189$ | $0.160$ |
|                            |             | $0.116 (±0.017)$ | $0.127$                           | $0.105 (±0.005)$     | $0.151$ | $0.125$ |
|                            |             | $0.064 (±0.008)$ | $0.127$                           | $0.077 (±0.010)$     | $0.151$ | $0.129$ |
|                            |             | $\Gamma$ | $-0.32 (±0.01)$ | $-0.255$ | $-0.30 (±0.01)$ | $-0.102$ | $-0.252$ |
|                            |             | $X_{1,2}$ | $-3.205 (±0.05)$ | $-3.33$ | $-3.12 (±0.05)$ | $-3.27$ | $-3.45$ |

| $\delta$ Band Extrema (eV) | $k_F$ (Å⁻¹) | $\bar{M} - \bar{\Gamma} - \bar{M}$ | $\bar{X} - \bar{\Gamma} - \bar{X}$ | +2% (tensile strain) | −2% (compressive strain) |
|----------------------------|-------------|------------------------------------|------------------------------------|---------------------|-------------------------|
|                            |             | $-0.66 (±0.02)$ | $-0.70$                           | $-0.68 (±0.02)$     | $-0.66$ | $-0.81$ |
|                            |             | $-0.82 (±0.02)$ | $\delta_2$: $-0.88 (±0.05)$     | $-0.88 (±0.05)$     | $-0.81$ | $-0.81$ |
|                            |             | $-1.09 (±0.02)$ | $\delta_3$: $-0.95 (±0.02)$     | $-0.95 (±0.02)$     | $-0.95$ | $-0.95$ |
|                            |             | $\delta_1$: $-0.90 (±0.02)$ | $-0.855$                           | $\delta_1$: $-0.59 (±0.08)$ | $-0.55$ | $-0.7$ |
|                            |             | $\delta_2$: $-0.82 (±0.02)$ | $\delta_2$: $-0.88 (±0.05)$     | $-0.88 (±0.05)$     | $-0.81$ | $-0.81$ |
|                            |             | $\delta_3$: $-1.09 (±0.02)$ | $\delta_3$: $-1.09 (±0.02)$     | $-1.09 (±0.02)$     | $-1.09$ | $-1.09$ |

| $\beta$ Band Extrema (eV) | $k_F$ (Å⁻¹) | $\bar{M} - \bar{\Gamma} - \bar{M}$ | $\bar{X} - \bar{\Gamma} - \bar{X}$ | +2% (tensile strain) | −2% (compressive strain) |
|----------------------------|-------------|------------------------------------|------------------------------------|---------------------|-------------------------|
|                            |             | $1.41 (±0.01)$ | $1.33$                           | $1.45 (±0.03)$     | $1.33$ | $1.48$ |
|                            |             | $1.70 (±0.05)$ | $\beta_2$: $1.70 (±0.05)$     | $-1.33$ | $-1.48$ |
|                            |             | $1.31 (±0.02)$ | $\beta_3$: $1.31 (±0.02)$     | $-1.18$ | $-1.33$ |
|                            |             | $\beta_1$: $1.41 (±0.01)$ | $-1.45$                           | $\beta_1$: $1.41 (±0.01)$ | $-1.45$ | $-1.45$ |

| $\gamma$ Band Extrema (eV) | $k_F$ (Å⁻¹) | $\bar{M} - \bar{\Gamma} - \bar{M}$ | $\bar{X} - \bar{\Gamma} - \bar{X}$ | +2% (tensile strain) | −2% (compressive strain) |
|----------------------------|-------------|------------------------------------|------------------------------------|---------------------|-------------------------|
|                            |             | $-3.205 (±0.05)$ | $-3.33$                           | $-3.12 (±0.05)$     | $-3.27$ | $-3.45$ |

Confinement effects

DFT calculations in Figure S1 modeling the effect of quantum confinement in 13 ML of GdSb (001) slabs show that the electron pockets in the film plane are experiencing quantum confinement, in contrast to the electron bands lying in the [001] direction. The pockets in the film plane normal direction do not experience quantum confinement, at least not to the same extent as their in-plane counterparts, due to their in-plane orbital composition, see Figure 4. The 4 nm strained GdSb films showed an experimental shift in the $\gamma$ hole band by $\sim$ 0.1 eV away from the Fermi level and reduced Fermi wave
vectors in both the light- and heavy-hole bands along \( \overline{X} - \overline{\Gamma} - \overline{X} \) compared to the bulk-limit 20-nm-thick unstrained film\(^{16} \). The electron pocket second quantum well state at \( \overline{M} \) is predicted to nearly graze the Fermi level in our calculation in Figure S1 but experimentally lies well below the Fermi level in Figure 2(b). The smaller quantum well state spacing is most likely due to the finite potential barrier at the film-substrate/buffer layer interface, whereas our calculation assumes a freestanding GdSb slab.

**Figure S1.** DFT-calculated electronic structure of free-standing GdSb (001) films that are 13ML thick for (a) 2% compressively strained, (b) unstrained, and (c) 2% tensile strained films. The electron pockets lying in the film plane (X\(_{1,2}\), projecting to \( \overline{M} \) shift to higher energies compared to the electron pockets in the film plane normal direction (Z, projecting to \( \overline{\Gamma} \)), with an energy difference of 124 meV calculated for the unstrained film.

II. **Supp. Info II**

**Tight binding model construction: hopping parameters and Hamiltonian construction**

Our orbital composition determination in Figure 4 shows the \( p \)-and \( d \)-orbital composition of the valence and conduction band, respectively, and agrees with ARPES measurements by Nummy et al.\(^{12} \) assigning the orbital characters in the analogous La-Vs. In addition, we do not observe significant mixing between \( s \) orbitals and the group of \( p \) and \( d \) orbitals near the Fermi level. The TB Hamiltonian is thus constructed by 16 x 16 matrix elements, consisting of 8 atomic orbitals (Sb: \( p_x, p_y, p_z \); and Gd: \( d_{yz}, d_{zx}, d_{xy}, d_{x^2-y^2}, d_{z^2} \)) and accounting for spin-orbit coupling (SOC) which contains the atomic SOC
parameter $\lambda_{\text{Gd}}$ and $\lambda_{\text{Sb}}$. These parameters are matched to the Gd 5$d$ and Sb 5$p$ atomic values, which are $\lambda_{\text{Gd}}=0.43$ eV and $\lambda_{\text{Sb}}=0.53$ eV.$^{17}$ On-site energies are derived from the unstrained GdSb calculation: $\text{Sb}_p=4.190$ eV, $\text{Gd}_d(e_g)= 9.283$ eV, and $\text{Gd}_d(t_{2g})= 7.562$ eV.

Taking the two-center approximation and considering only the nearest-neighbor Gd-Sb interactions and the next nearest-neighbor Gd-Gd and Sb-Sb interatomic couplings, the hopping terms are expressed by.$^{18}$

$$t(p_x,p_y)[110]=1/2 \left( p_{\text{Sb}} p_{\text{Sb}} \sigma - p_{\text{Sb}} p_{\text{Sb}} \pi \right)$$

$$t(p_x,p_x)[110]=1/2 \left( p_{\text{Sb}} p_{\text{Sb}} \sigma + p_{\text{Sb}} p_{\text{Sb}} \pi \right)$$

$$t(p_{x,y},d_{xy})_{[100]/[010]} = p_{\text{Sb}} d_{\text{Gd}} \pi$$

$$t(d_{xy},d_{xy})_{[110]}=1/4 \left( 3d_{\text{Gd}} d_{\text{Gd}} \sigma + d_{\text{Gd}} d_{\text{Gd}} \delta \right)$$

$$t(d_{xy},d_{xy})_{[011]}=1/2 \left( d_{\text{Gd}} d_{\text{Gd}} \pi + d_{\text{Gd}} d_{\text{Gd}} \delta \right)$$

$$t(d_{xy},d_{yz})_{[101]}=1/2 \left( d_{\text{Gd}} d_{\text{Gd}} \pi - d_{\text{Gd}} d_{\text{Gd}} \delta \right)$$

$$t(p_{x,y},d_{x^2-y^2})_{[100]/[010]} = \frac{\sqrt{3}}{2} p_{\text{Sb}} d_{\text{Gd}} \sigma$$

The obtained TB parameters in the standard Slater-Koster notation are tabulated in Table S2. The Fermi level was set to 5.6 eV so that the DFT and TB dispersions match in position for unstrained GdSb.

Using the parameters listed in Table S2, the TB model is constructed using the open-source package chinook.$^{19}$ The energy dispersion obtained from the TB model in Figure 4(d) and Figure S2 reproduces well the ARPES and DFT results. Being isotropic, the TB model accounts for the strain-induced changes in hopping terms by using Slater-Koster parameters derived primarily from hopping terms in the (001) plane (except $t(d_{xy},d_{xy})_{[011]}$ and $t(d_{xy},d_{yz})_{[101]}$ in order to extract $d_{\text{Gd}} d_{\text{Gd}} \pi$ and $d_{\text{Gd}} d_{\text{Gd}} \delta$).

The hopping term decay rate, $V^* - V_0$, is calculated based on the absolute difference between the strained ($V^*$) and unstrained ($V_0$) hopping terms. For example, $V(p_{\text{Sb}} p_{\text{Sb}} \pi)^{+2\%} - V(p_{\text{Sb}} p_{\text{Sb}} \pi)^{0\%} = -0.064 - (-0.090) = 0.026$. 

7
Table S2. Nearest- and next-nearest neighbors TB parameters for GdSb, extracted from DFT calculations.

| Parameters (eV)/Strain | −2% | 0%  | +2%  |
|------------------------|-----|-----|------|
| p_Sb p_Sb σ            | 0.713 | 0.661 | 0.583 |
| p_Sb p_Sb π            | −0.095 | −0.090 | −0.064 |
| d_Gd d_Gd σ            | −0.814 | −0.745 | −0.695 |
| d_Gd d_Gd π            | 0.233 | 0.239 | 0.238 |
| d_Gd d_Gd δ            | 0.051 | 0.046 | 0.056 |
| p_Sd d_Gd π            | −0.964 | −0.894 | −0.845 |
| p_Sd d_Gd σ            | −1.899 | −1.745 | −1.665 |
| λ_Gd                   | 0.43 |
| λ_Sb                   | 0.53 |

Figure S2. Wide energy range $E$-$k$ dispersion based on the constructed TB model for unstrained GdSb.

III. Supp. Info III

Magnetic properties of strained GdSb films

GdSb can be considered an orbitally quenched system since the 4$f^7$ configuration results in zero orbital angular momentum. Therefore, there is a negligible crystalline electric field (CEF) effect. The weak CEF effect in GdSb permits us to overlook the impact of strain on the local symmetry breaking and to easily elucidate the role strain-driven band structure modifications and orbital overlap might have on magnetic ordering in GdSb. The 4$f$ electrons in GdSb are well localized, with occupied states at 8.7
eV below the Fermi level\textsuperscript{20}. Super-exchange interactions (via \(p\)-\(d\) hopping in Gd-Sb) and Ruderman-Kittel-Kasuya-Yosida (RKKY) indirect-exchange interactions are expected to coexist in this compound\textsuperscript{21}, the former leading to antiferromagnetic behavior, and the latter contributing to a competing ferromagnetic order. Assuming a molecular field approximation can describe well the ordering in GdSb\textsuperscript{22}, the Néel Temperature (\(T_N\)) of a type II Heisenberg AFM with \(S=7/2\) is\textsuperscript{23}:

\[
k_B T_N = \frac{2}{3} S(S + 1) \hbar^2 (-6J_2) = -63 \hbar^2 J_2
\]

\(J_2\) being the next nearest neighbor exchange constant. The pnictogen \(p\)-orbitals mediate the AFM super-exchange interactions between the Gd atoms, and \(J_2\) can be expressed by the empirical relation used for transition-metal compounds:

\[
J_{2,\text{super}} = -\frac{n_d t_{pd}^4}{\Delta^2} \left( \frac{1}{U} + \frac{1}{\Delta} \right)
\]

where \(n_d\) is the \(d\) moment induced by intra-atomic \(5f\)-\(4d\) exchange, \(t_{pd}\) is the hopping integral between the Sb-\(p\) and Gd-\(d\) orbitals, \(U\) is the on-site coulomb energy and \(\Delta\) is the energy difference between the \(d\) and \(p\) orbitals\textsuperscript{21,24}. From Table S2, we can see that both \(t_{pd\sigma}\) and \(t_{pd\pi}\) hopping terms increase (in absolute value) moving from tensile to compressive strain, in agreement with the stronger superexchange interaction expected with decreasing lattice constant. A monotonic increase in \(T_N\) is measured as a function of strain. Figure S3 highlights the change in \(T_N\) as a function of film strain with a 2.6 °C difference measured. Similar strain-dependent changes were measured for EuTe, an \(S=7/2\) rare-earth analogue\textsuperscript{25}. However, the superexchange parameter \(J_2\) in GdSb is predicted to be much larger and more sensitive to variations in the lattice constant\textsuperscript{22}. 
Figure S3. Néel temperature in +2 and −2% strained 4-nm-thick GdSb films. (a) Temperature dependence of the longitudinal resistivity normalized to the maximum resistivity. At high temperatures >70 K, transport is dominated by the III-V substrate and/or buffer layer. Under 70 K, the charge carriers in the III-V buffer layer and GaSb substrate freeze out, and transport is dominated by the GdSb films. (b-c) Néel temperature extracted from a parabolic fit (black line) to the second derivative of the resistivity at B=0 T, for (b) +2% strain ($T_N=24.3$ K) and (c) −2% biaxial strain ($T_N=26.9$ K).

REFERENCES:

(1) Klemenz, S.; Lei, S.; Schoop, L. M. Topological Semimetals in Square-Net Materials. *Annu. Rev. Mater. Res.* **2019**, *49* (1), 185–206. https://doi.org/10.1146/annurev-matsci-070218-010114.

(2) Hohenberg, P.; Kohn, W. Inhomogeneous Electron Gas. *Phys. Rev.* **1964**, *136* (3B), B864–B871. https://doi.org/10.1103/PhysRev.136.B864.

(3) Kohn, W.; Sham, L. J. Self-Consistent Equations Including Exchange and Correlation Effects. *Phys. Rev.* **1965**, *140* (4A), A1133–A1138. https://doi.org/10.1103/PhysRev.140.A1133.

(4) Blöchl, P. E. Projector Augmented-Wave Method. *Phys. Rev. B* **1994**, *50* (24), 17953–17979. https://doi.org/10.1103/PhysRevB.50.17953.

(5) Popescu, V.; Zunger, A. Effective Band Structure of Random Alloys. *Phys. Rev. Lett.* **2010**, *104* (23), 236403. https://doi.org/10.1103/PhysRevLett.104.236403.

(6) Popescu, V.; Zunger, A. Extracting E versus k Effective Band Structure from Supercell Calculations on Alloys and Impurities. *Phys. Rev. B* **2012**, *85* (8), 085201. https://doi.org/10.1103/PhysRevB.85.085201.

(7) Rourke, P. M. C.; Julian, S. R. Numerical Extraction of de Haas–van Alphen Frequencies from
Calculated Band Energies. *Comput. Phys. Commun.* **2012**, *183* (2), 324–332. https://doi.org/10.1016/j.cpc.2011.10.015.

(8) Wu, Z.; Wu, F.; Li, P.; Guo, C.; Liu, Y.; Sun, Z.; Cheng, C. M.; Chiang, T. C.; Cao, C.; Yuan, H.; Liu, Y. Probing the Origin of Extreme Magnetoresistance in Pr/Sm Mono-Antimonides/Bismuthides. *Phys. Rev. B* **2019**, *99* (3), 035158. https://doi.org/10.1103/PhysRevB.99.035158.

(9) He, J.; Zhang, C.; Ghimire, N. J.; Liang, T.; Jia, C.; Jiang, J.; Tang, S.; Chen, S.; He, Y.; Mo, S.-K.; Hwang, C. C.; Hashimoto, M.; Lu, D. H.; Moritz, B.; Devereaux, T. P.; Chen, Y. L.; Mitchell, J. F.; Shen, Z.-X. Distinct Electronic Structure for the Extreme Magnetoresistance in YSb. *Phys. Rev. Lett.* **2016**, *117* (26), 267201. https://doi.org/10.1103/PhysRevLett.117.267201.

(10) Kuroda, K.; Ochi, M.; Suzuki, H. S.; Hirayama, M.; Nakayama, M.; Noguchi, R.; Bareille, C.; Akebi, S.; Kunisada, S.; Muro, T.; Watson, M. D.; Kitazawa, H.; Haga, Y.; Kim, T. K.; Hoesch, M.; Shin, S.; Arita, R.; Kondo, T. Experimental Determination of the Topological Phase Diagram in Cerium Monopnictides. *Phys. Rev. Lett.* **2018**, *120* (8), 086402. https://doi.org/10.1103/PhysRevLett.120.086402.

(11) Yang, H.-Y.; Nummy, T.; Li, H.; Jaszewski, S.; Abramchuk, M.; Dessau, D. S.; Tafti, F. Extreme Magnetoresistance in the Topologically Trivial Lanthanum Monopnictide LaAs. *Phys. Rev. B* **2017**, *96* (23), 235128. https://doi.org/10.1103/PhysRevB.96.235128.

(12) Nummy, T. J.; Waugh, J. A.; Parham, S. P.; Liu, Q.; Yang, H.-Y.; Li, H.; Zhou, X.; Plumb, N. C.; Tafti, F. F.; Dessau, D. S. Measurement of the Atomic Orbital Composition of the Near-Fermi-Level Electronic States in the Lanthanum Monopnictides LaBi, LaSb, and LaAs. *npj Quantum Mater.* **2018**, *3* (1), 24. https://doi.org/10.1038/s41535-018-0094-3.

(13) Wu, Y.; Lee, Y.; Kong, T.; Mou, D.; Jiang, R.; Huang, L.; Bud’Ko, S. L.; Canfield, P. C.; Kaminski, A. Electronic Structure of RSb (R= Y, Ce, Gd, Dy, Ho, Tm, Lu) Studied by Angle-Resolved Photoemission Spectroscopy. *Phys. Rev. B* **2017**, *96* (3), 035134. https://doi.org/10.1103/PhysRevB.96.035134.

(14) Duan, X.; Wu, F.; Chen, J.; Zhang, P.; Liu, Y.; Yuan, H.; Cao, C. Tunable Electronic Structure and Topological Properties of LnPn (Ln=Ce, Pr, Sm, Gd, Yb; Pn=Sb, Bi). *Commun. Phys.* **2018**, *1* (1), 71. https://doi.org/10.1038/s42005-018-0074-8.

(15) Chao, C. Y.-P.; Chuang, S. L. Spin-Orbit-Coupling Effects on the Valence-Band Structure of Strained Semiconductor Quantum Wells. *Phys. Rev. B* **1992**, *46* (7), 4110–4122. https://doi.org/10.1103/PhysRevB.46.4110.

(16) Inbar, H. S.; Ho, D. Q.; Chatterjee, S.; Pendharkar, M.; Engel, A. N.; Dong, J. T.; Khalid, S.; Chang, Y. H.; Guo, T.; Fedorov, A. V.; Lu, D.; Hashimoto, M.; Read, D.; Janotti, A.; Palmstrøm, C. J. Epitaxial Growth, Magnetoresistance, and Electronic Band Structure of GdSb Magnetic Semimetal Films. *2022*.

(17) Herman, F.; Skillman, S. *Atomic Structure Calculations*; Prentice-Hall: Englewood Cliffs, New Jersey, 1963.

(18) Slater, J. C.; Koster, G. F. Simplified LCAO Method for the Periodic Potential Problem. *Phys.
(19) Day, R. P.; Zwartsenberg, B.; Elfimov, I. S.; Damascelli, A. Computational Framework Chinook for Angle-Resolved Photoemission Spectroscopy. *npj Quantum Mater.* **2019**, *4* (1), 54. https://doi.org/10.1038/s41535-019-0194-8.

(20) Yamada, H.; Fukawa, T.; Muro, T.; Tanaka, Y.; Imada, S.; Suga, S.; Li, D.-X.; Suzuki, T. XPS and X-BIS Studies of Gd Monopnictides. *J. Phys. Soc. Japan* **1996**, *65* (4), 1000–1004. https://doi.org/10.1143/JPSJ.65.1000.

(21) Duan, C.-G.; Sabiryanov, R. F.; Mei, W. N.; Dowben, P. A.; Jaswal, S. S.; Tsymbal, E. Y. Magnetic Ordering in Gd Monopnictides: Indirect Exchange versus Superexchange Interaction. *Appl. Phys. Lett.* **2006**, *88* (18), 182505. https://doi.org/10.1063/1.2200767.

(22) Li, D. X.; Haga, Y.; Shida, H.; Suzuki, T.; Kwon, Y. S.; Kido, G. Magnetic Properties of Stoichiometric Gd Monopnictides. *J. Phys. Condens. Matter* **1997**, *9* (48), 10777–10788. https://doi.org/10.1088/0953-8984/9/48/019.

(23) Nolting, W.; Ramakanth, A. *Quantum Theory of Magnetism*; Springer Berlin Heidelberg: Berlin, Heidelberg, 2009. https://doi.org/10.1007/978-3-540-85416-6.

(24) Zaanen, J.; Sawatzky, G. A. The Electronic Structure and Superexchange Interactions in Transition-Metal Compounds. *Can. J. Phys.* **1987**, *65* (10), 1262–1271. https://doi.org/10.1139/p87-201.

(25) Kępa, H.; Springholz, G.; Giebultowicz, T. M.; Goldman, K. I.; Majkrzak, C. F.; Kacman, P.; Blinowski, J.; Holl, S.; Krenn, H.; Bauer, G. Magnetic Interactions in EuTe Epitaxial Layers and EuTe/PbTe Superlattices. *Phys. Rev. B* **2003**, *68* (2), 024419. https://doi.org/10.1103/PhysRevB.68.024419.