

Magnetic Ordering and Bonding in Ln_3TiBi_5 ($\text{Ln} = \text{Pr}, \text{Nd}, \text{Gd}$)

Published as part of ACS Materials Au special issue “2026 Rising Stars in Materials Science”.

Kaige Wu,^{||} Danila S. Sokratov,^{||} Ram Kumar, Hope A. Long, Johnpierre Paglione, and Vladislav V. Klepov^{*}



Cite This: <https://doi.org/10.1021/acsmaterialsau.6c00162>



Read Online

ACCESS |



Metrics & More



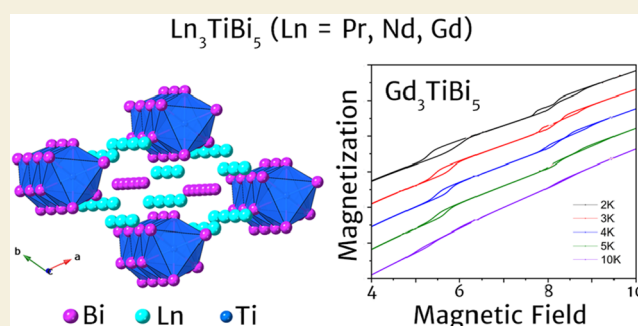
Article Recommendations



Supporting Information

ABSTRACT: Topological materials have gained remarkable attention due to their exotic properties and potential applications in advanced devices. The Ln_3MPn_5 ($\text{Ln} = \text{lanthanide}$, $\text{M} = \text{transition metal}$, $\text{Pn} = \text{pnictide}$) family, which hosts hypervalent Bi chains, has been identified as a promising platform to study magnetic topological materials. Herein, we present single-crystal growth of new compounds Ln_3TiBi_5 ($\text{Ln} = \text{Pr}, \text{Nd}, \text{and Gd}$) and their property characterization. Magnetic measurements on Pr_3TiBi_5 show no apparent indications of magnetic ordering down to 2 K, whereas both Nd_3TiBi_5 and Gd_3TiBi_5 show antiferromagnetic ordering at 6.2 and ~ 18 K, respectively. Gd_3TiBi_5 exhibits antiferromagnetic transitions at 17.1 K ($H \parallel c$) and 18.8 K ($H \perp c$), respectively, suggesting competing ground states of this compound. Heat capacity measurements on the samples confirm the presence of magnetic ordering. DFT calculations reveal band crossings that are located above the Fermi level in Pr_3TiBi_5 and Nd_3TiBi_5 , while the band structure of Gd_3TiBi_5 exhibits topologically nontrivial states near the Fermi level. In the presence of SOC, the electronic structure of Gd_3TiBi_5 changes dramatically. In particular, a local gap opens at the band crossing along $\text{M}-\text{K}$, and the band crossing along $\Gamma-\text{A}$ moves above the Fermi level. The crystal orbital Hamilton population (COHP) calculations illustrate the bonding character of $\text{Ln}-\text{Bi}_{6g}$, $\text{Ln}-\text{Bi}_{4d}$, $\text{Ti}-\text{Bi}_{6g}$, $\text{Bi}_{4d}-\text{Bi}_{4d}$, and $\text{Ti}-\text{Ti}$ in Ln_3TiBi_5 ($\text{Ln} = \text{Pr}, \text{Nd}, \text{Gd}$). Ln forms the strongest bonds with Bi_{6g} , followed by $\text{Ti}-\text{Bi}_{6g}$ and $\text{Ln}-\text{Bi}_{4d}$. $\text{Bi}_{4d}-\text{Bi}_{4d}$ in 1D Bi^{2-} chains forms hypervalent bonding, with both bonding and antibonding states below the Fermi level. $\text{Ti}-\text{Ti}$ interactions are relatively weak compared with the other bonding interactions. This work fills the gap in the Ln_3TiBi_5 family with the synthesis of Pr_3TiBi_5 and Nd_3TiBi_5 and also extends it to Gd_3TiBi_5 , the first Gd-containing compound in the anti- $\text{Hf}_5\text{Sn}_3\text{Cu}$ -type series.

KEYWORDS: hypervalent bonding, topological materials, magnetism, bismuth, lanthanides



INTRODUCTION

Topological semimetals (TSMs) are a class of gapless quantum materials exhibiting protected band crossing in the bulk band structure and vanished density of states near the Fermi energy.^{1–4} The most common TSMs are Dirac semimetals (DSMs) and Weyl semimetals (WSMs).^{5–8} DSMs possess a Dirac point formed by the crossing of two sets of linearly dispersed bands at a single point.⁹ The two sets of bands are 2-fold degenerate, making a Dirac point 4-fold degenerate.⁸ The breaking of either inversion symmetry or time-reversal symmetry in DSMs results in WSMs,^{4,10,11} which exhibit a crossing of non-degenerate bands.^{12–14} The crossing of linearly dispersed bands in the bulk is a defining feature of TSMs, which leads to the emergence of massless Dirac and Weyl Fermions.^{4,15} Because of the “massless” nature, a distinguished feature of Dirac and Weyl Fermions is their ultrafast mobility,^{9,16–19} giving rise to a series of exotic phenomena such as a huge magneto-resistance effect,^{20–22} quantum Hall effect,²³ quantum oscillations,²⁴ etc. Apart from that, linear band dispersion also

induces exotic optical properties like optical conductivity and long-wavelength photon absorption.^{9,25,26} In addition, nonlinear optical effects have been noticeable in WSMs with chiral crystal structures.^{27,28} Due to these distinguishing properties, TSMs hold significant promise in applications for spintronics, catalysis, and optical devices.^{29–34} TSMs opened a pathway to a new class of quantum materials, which has sparked a tremendous interest in predicting and discovering new TSMs among condensed matter physics and solid-state chemistry communities.^{35–38}

Despite an abundance of computationally predicted topological materials, their realization remains a challenge due to

Received: June 26, 2026

Revised: August 13, 2026

Accepted: August 14, 2026

difficulties in their characterization. While first-principles calculations have been at the forefront of revealing nontrivial topology in the electronic structures of materials,^{39–41} angle-resolved photoemission spectroscopy (ARPES) remains a primary experimental technique in verifying topological phases owing to its unique ability to directly probe the electronic structure with energy and momentum resolution.^{42–45} Recently, Schoop et al. introduced simple chemical design rules that allow for predicting TSM properties in materials from a chemist's perspective, enabling the synthesis of new topological phases based on structural considerations.⁴⁶ One of the two requirements is that the unit cell of TSM candidate should contain two chemically equivalent atoms, which enables band folding and leads to band inversion and band crossing, a primary source for a topological phase.^{46,47} The second requirement is the presence of extended multicenter hypervalent bonds, where electrons delocalize over a structural motif, enabling its partial electron filling.^{46–48} It was proposed by Hoffmann to explain several networks of heavy p-group elements that are against the Zintl–Klemm electron-precise rule.⁴⁸ The hypervalent bonds can not only stabilize the topological band structure for a half-filled band and thus locate the Fermi level to the crossing point by avoiding Peierls distortion but also enhance the material's tolerance to defects that would alter the position of Fermi level through the formation of steep and widely dispersed bands.^{46,47,49–51}

One motif that follows the chemical rules for TSMs is the 1D Bi^{2-} chain in Ln_3MPn_5 (Ln = lanthanide or actinide, M = transition metal, Pn = Sb or Bi) compounds crystallizing in the anti- $\text{Hf}_5\text{Sn}_3\text{Cu}$ -type, and it has been identified as a suitable platform to study topological materials.⁵¹ In this structure type, each chain contains two Pn atoms within the unit cell, enabling band folding.⁵¹ The seven electrons per Pn^{2-} anion lead to a half-filled p_z orbital per Pn atom and electron-rich, multicenter hypervalent bonding.^{49,51} The half-filled orbitals pin the Fermi level at the crossing point in the folded band structures.⁵¹ The hypervalent bonding stabilizes the half-filled orbitals and thus protects the band structure that would form an energy gap due to the Peierls distortion.^{49,51} A unit cell has two chains, the interaction of which finally brings about a topological band structure.⁵¹ One example of such compounds is Sm_3ZrBi_5 , which has been recently identified as a new magnetic topological material. Despite significant synthetic efforts toward the synthesis of new bismuthide materials, there are still gaps in the composition phase space that limit our understanding of the stability ranges and properties in this promising class of materials, necessitating the discovery and single-crystal growth of new members of this family.

To extend the family of potential topological phases, we focus on the Ln_3TiBi_5 (Ln = lanthanide) anti- $\text{Hf}_5\text{Sn}_3\text{Cu}$ -type family of compounds, in which only Ln = La, Ce, and Sm phases have been reported.^{52–55} The size of lanthanides significantly affects the stability of Ln_3MPn_5 phases, with early lanthanides, La^{3+} – Sm^{3+} , favoring this structure type, whereas the remaining lanthanides tend to form ternaries with other structure types.^{49,56–62} In this report, we not only fill the gap in the Ln_3TiBi_5 family by synthesizing Pr_3TiBi_5 and Nd_3TiBi_5 but also extend it to Gd_3TiBi_5 , the first Gd-containing compound in the anti- $\text{Hf}_5\text{Sn}_3\text{Cu}$ -type structure. The synthesis of high-quality single crystals of three new members in Ln_3TiBi_5 (Ln = Pr, Nd, Gd) enables the characterization of their structural and magnetic properties. The experimental data are corroborated by a detailed computational study that reveals the features of their electronic structures.

RESULTS AND DISCUSSION

Crystal Growth and Crystal Structure

Large, mm-scale crystals of Ln_3TiBi_5 (Ln = Pr, Nd, and Gd; Figure 1c–e) were grown via self-flux reactions where Ln and Ti

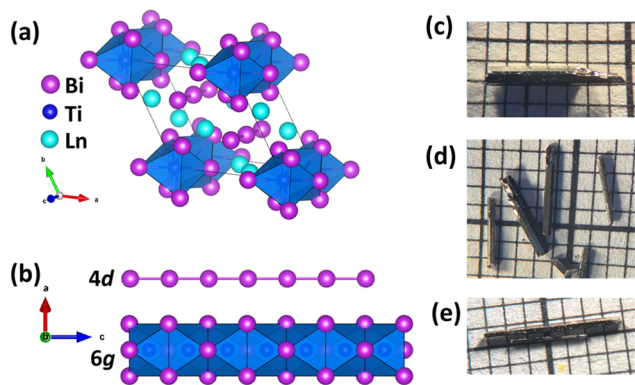


Figure 1. Crystal structure of Ln_3TiBi_5 (Ln = Pr, Nd, and Gd). (a) Individual unit cell shown along the c direction. (b) Separate 1D Bi^{2-} motif (top) and 1D TiBi_6 octahedra motif (bottom). Optical microscope images of (c) Pr_3TiBi_5 , (d) Nd_3TiBi_5 , and (e) Gd_3TiBi_5 , respectively, on a millimeter paper.

were reacted in the molar ratio of 3:1 and excess Bi was employed as flux.^{63–65} For Ln_3TiBi_5 (Ln = Pr, Nd), the reaction temperature was 900 °C. In the synthesis of Gd_3TiBi_5 , a significant amount of plate-like Kagome phase GdTi_3Bi_4 ⁶⁶ formed along with Gd_3TiBi_5 at 900 °C, so the temperature was set to 750 °C to reduce the amount of the side product.

As shown in Figure 1 and Table S1, Ln_3TiBi_5 (Ln = Pr, Nd, Gd) crystallizes in the space group $P6_3/mcm$ and the anti- $\text{Hf}_5\text{Sn}_3\text{Cu}$ structure type. 1D Bi^{2-} chains and 1D face-sharing TiBi_6 octahedra run along the c axis, charge balanced by Ln^{3+} (Ln = Pr, Nd, Gd). Bi atoms occupy two different Wyckoff positions; 4d positions contain Bi^{2-} chain atoms, and the 6g Bi atoms form TiBi_6 octahedra (Figure 1b).

To better understand the structure of this family, we list the bond lengths of Bi–Bi and M–Bi in Ln_3MBi_5 (Ln = La, Ce, Pr, Nd, Sm, Gd; M = Sc, Ti, Mn, Zr, Hf, Mg)^{49,51,52,58,67–69} in Table S2. All the Bi–Bi bond lengths in the chains lie within a 3.17–3.28 Å range and are longer than elemental Bi (~ 3.07 Å), suggesting the existence of hypervalent bonds.^{51–53} Seven electrons per atom in the Bi^{2-} chains lead to electron-rich multicenter bonding (hypervalent bonding).^{48,49,51,52} Each Bi atom in Bi^{2-} chains contains filled s , p_x , p_y orbitals, and a half-filled p_z orbital.^{49,51} The half-filled p_z orbitals bring about one electron each to the hypervalent bond, causing longer Bi–Bi lengths than two-center two-electron bonds, which have more localized interactions.^{47–49,51} With the same M in Ln_3MBi_5 , Bi–Bi and M–Bi bond lengths shorten as the radius of lanthanides becomes smaller (Figure S1a). For example, Bi–Bi and M–Bi bond lengths reduce from 3.2010 and 2.9301 Å in Pr_3TiBi_5 to 3.1719 and 2.9234 Å in Gd_3TiBi_5 , respectively, which agrees with lanthanide contraction. Similarly, a comparison of the Bi–Bi and M–Bi bond lengths in Ln_3MBi_5 (M = Ti, Zr, Hf) with the same Ln also shows the expected trends due to secondary periodicity due to lanthanide contraction (Figure S1a).⁴⁹ The bond lengths in Ln_3TiBi_5 are shorter than those in Ln_3ZrBi_5 as Zr has a larger radius (Figure S1), but the transition to Ln_3HfBi_5 results in only slightly longer bonds. A similar trend is found in Ln_3MSb_5 with the same Ln (Ln = La, Ce, Pr, Nd, Sm; M = Ti, Zr,

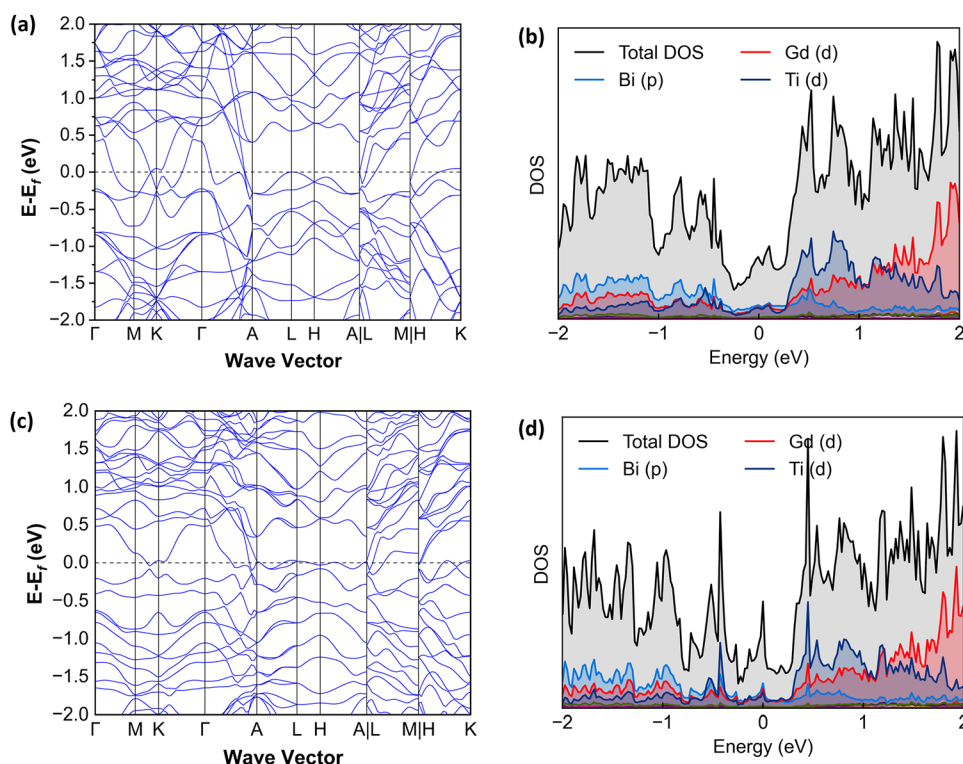


Figure 2. Electronic structure of Gd_3TiBi_5 . (a) Band structure of Gd_3TiBi_5 without spin–orbit coupling. (b) Density of states of Gd_3TiBi_5 without spin–orbit coupling. (c) Band structure of Gd_3TiBi_5 with spin–orbit coupling. (d) Density of states of Gd_3TiBi_5 with spin–orbit coupling.

Hf),⁶² in which Ln_3ZrSb_5 has the longest bond lengths of Sb–Sb and M–Sb, followed by Ln_3HfSb_5 and Ln_3TiSb_5 (Figure S1b and Table S3), except for the Sb–Sb bond length in La_3TiSb_5 .

The size of lanthanides significantly affects the stability of Ln_3MPn_5 phases.⁴⁹ Khoury et al. proposed a comprehensive diagram of phase stability in this family by collating a structural map of known Ln_3MPn_5 compounds and found that early lanthanides, La^{3+} – Sm^{3+} , and U^{3+} favor the Ln_3MPn_5 composition, whereas lanthanides smaller than Sm^{3+} tend to form ternaries with other structure types.⁴⁹ Although Pr_3TiBi_5 and Nd_3TiBi_5 fall well within the proposed stability range of the Ln_3MPn_5 type, the synthesis of Gd_3TiBi_5 suggests that more compounds with smaller lanthanide atoms can be obtained, further extending this structure type.

Electronic Structure

The band structures of Pr_3TiBi_5 and Nd_3TiBi_5 calculated without spin–orbit coupling (SOC) exhibit band crossings above the Fermi level along the Γ –A path (Figures S2 and S3). Gd_3TiBi_5 , without SOC (Figure 2a), features topological band crossing⁵¹ near the Fermi level along M–K and Γ –A high-symmetry lines. The two band crossings, however, stem from distinct contributions of p orbitals at the 4d and 6g Wyckoff positions of Bi, which is revealed by orbital-projected band structures for Gd_3TiBi_5 (Figures S4–S6). The band crossing near the Fermi level along the M–K path is mainly derived from p_x and p_y orbitals of Bi at the 6g Wyckoff position, with significantly weaker contributions from p_x and p_y orbitals of Bi at the 4d Wyckoff position and no involvement of the p_z orbital from either site. In contrast, the band crossing near the Fermi level along the Γ –A direction is predominantly contributed by p orbitals of Bi at the 4d Wyckoff position, in which the p_z orbital plays the leading role. A smaller contribution comes from p_x and p_y orbitals of Bi at 6g and 4d Wyckoff positions. This analysis

indicates that Bi atoms in both the Bi–Bi chains and TiBi_6 octahedra play a crucial role in establishing the overall topological character of the band structure. The band crossing along Γ –A exhibits a steeper dispersion than that along the M–K direction, indicating greater robustness to SOC-induced gaps. This is demonstrated by the band structure of Gd_3TiBi_5 with SOC (Figure 2c), where a local gap of around 0.044 eV opens along the M–K direction. While the local energy gap is smaller than that of most known topological insulators, it remains significant.⁵¹ In contrast, SOC induces no local gap for the band crossing along Γ –A. Instead, it shifts the band crossing upward to approximately 0.44 eV above the Fermi level. Additionally, SOC shifts the degeneracy at the A point closer to the Fermi level, and a degeneracy at the L point emerges near the Fermi level.

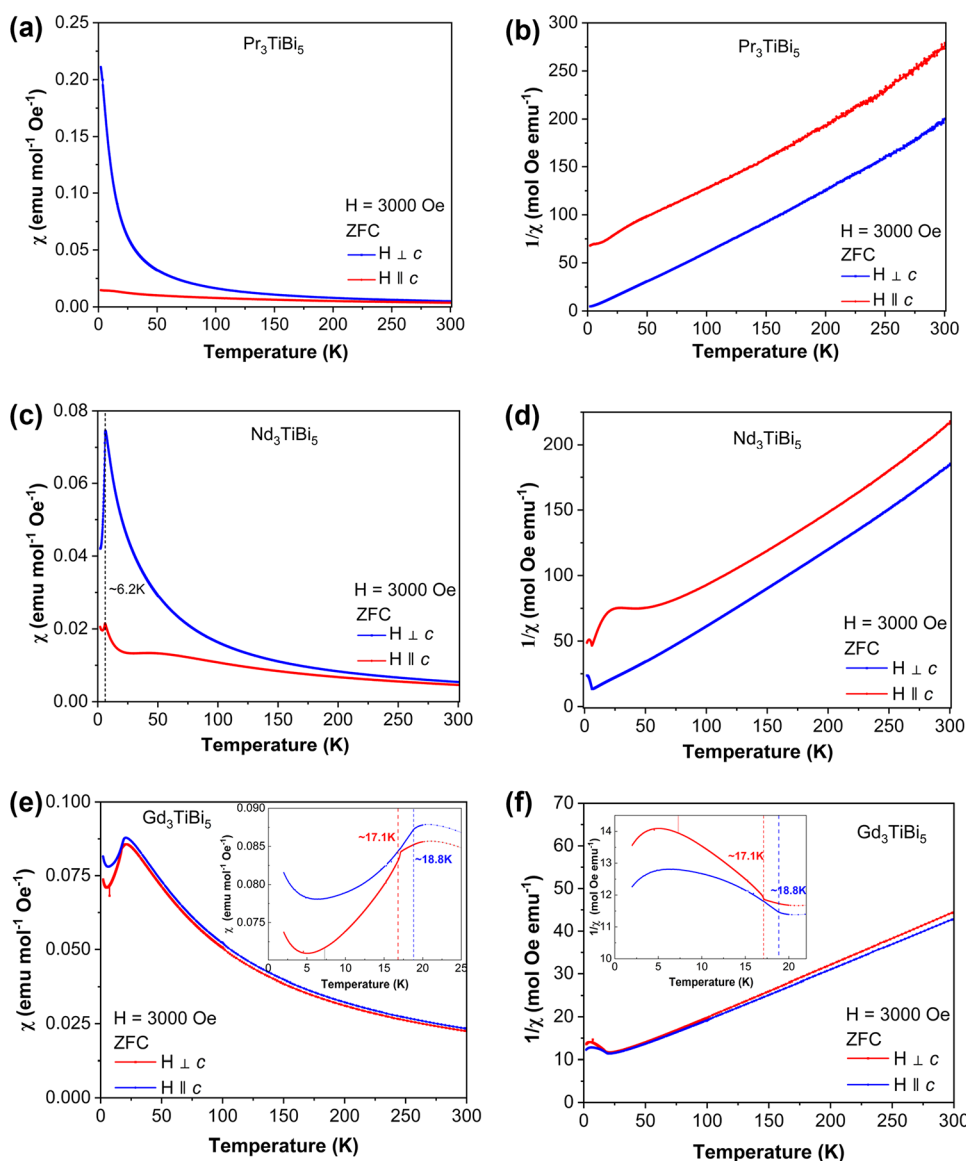
Both the total and partial density of states (DOS), without and with SOC (Figure 2b,d), show that Bi p, Ti d, and Gd d orbitals contribute the most to the Fermi level. Furthermore, the DOS peaks with SOC are sharper than those without SOC, which can be attributed to SOC-induced band flattening. As observed in the band structure (Figure 2c), SOC reduces band dispersion, resulting in flatter bands and consequently a higher density of states at the Fermi level (Figure 2d). A higher density of states can enhance electron–electron interactions, leading to stronger electronic correlations, which may give rise to the emergence of exotic physical phenomena.⁷⁰ Overall, the electronic behavior of Gd_3TiBi_5 is similar to Sm_3ZrBi_5 .⁵¹

To get insights into the bonding features of Ln_3TiBi_5 ($\text{Ln} = \text{Pr}, \text{Nd}, \text{Gd}$), we calculated the crystal orbital Hamilton population (COHP). The optimized bond distances and integrated –COHP (–ICOHP) are listed in Table 1. As shown in Figures S7–S9, the interactions of Ln and Bi at the 6g Wyckoff position (Pr–Bi_{6g} , Nd–Bi_{6g} , Gd–Bi_{6g}) are strongly bonding, with all

Table 1. Selected Interactions along with Optimized Bond Distances and Corresponding $-ICOHP$ of Ln_3TiBi_5 ($Ln = Pr, Nd, Gd$)

compound	interaction	distance (Å)	$-ICOHP$ per bond (eV)
Pr_3TiBi_5	$Pr-Bi_{6g}$	3.272	2.21
	$Pr-Bi_{4d}$	3.448	1.52
	$Ti-Bi_{6g}$	2.961	1.64
	$Bi_{4d}-Bi_{4d}$	3.232	1.26
	$Ti-Ti$	3.232	0.65
Nd_3TiBi_5	$Nd-Bi_{6g}$	3.256	2.21
	$Nd-Bi_{4d}$	3.431	1.53
	$Ti-Bi_{6g}$	2.958	1.64
	$Bi_{4d}-Bi_{4d}$	3.222	1.26
	$Ti-Ti$	3.222	0.67
Gd_3TiBi_5	$Gd-Bi_{6g}$	3.212	1.81
	$Gd-Bi_{4d}$	3.380	1.27
	$Ti-Bi_{6g}$	2.947	1.60
	$Bi_{4d}-Bi_{4d}$	3.194	1.25
	$Ti-Ti$	3.194	0.70

bonding status below the Fermi level and $-ICOHP$ of 2.21, 2.21, and 1.81 eV/bond, respectively. The optimized distances of Ln to Bi at the $4g$ Wyckoff position ($Pr-Bi_{4d}$, $Nd-Bi_{4d}$, $Gd-Bi_{4d}$) are 3.448, 3.431, and 3.380 Å, respectively, longer than that of corresponding $Ln-Bi_{6g}$ (3.272, 3.256, and 3.212 Å), resulting in weaker but still strongly bonding with $-ICOHP$ of 1.52, 1.53, and 1.27 eV/bond, respectively. $Ln-Bi_{4d}$ ($Ln = Pr, Nd, Gd$) interactions are bonding below the Fermi level (Figures S7–S9). The $Ti-Bi_{6g}$ interactions are strongly bonding, with $-ICOHP$ values of 1.64, 1.64, and 1.60 eV/bond, respectively. They also show predominant bonding below the Fermi level (Figures S7–S9). The COHP curve of $Bi_{4d}-Bi_{4d}$ (Figures S7–S9) within the 1D Bi chains in Ln_3TiBi_5 exhibits both bonding and antibonding below the Fermi level, which is characteristic of hypervalent interactions in metal pnictides.⁷¹ The $Bi_{4d}-Bi_{4d}$ interactions are overall bonding, as evidenced by the $-ICOHP$ values of 1.26, 1.26, and 1.25 eV/bond, respectively. The $Ti-Ti$ interactions in Ln_3TiBi_5 are weaker than other interactions, with $-ICOHP$ values of 0.65, 0.67, and 0.70 eV/bond, respectively, but still

**Figure 3.** Magnetic susceptibility vs temperature plots of (a) Pr_3TiBi_5 , (c) Nd_3TiBi_5 , and (e) Gd_3TiBi_5 . Inverse magnetic susceptibility vs temperature plots of (b) Pr_3TiBi_5 , (d) Nd_3TiBi_5 , and (f) Gd_3TiBi_5 .

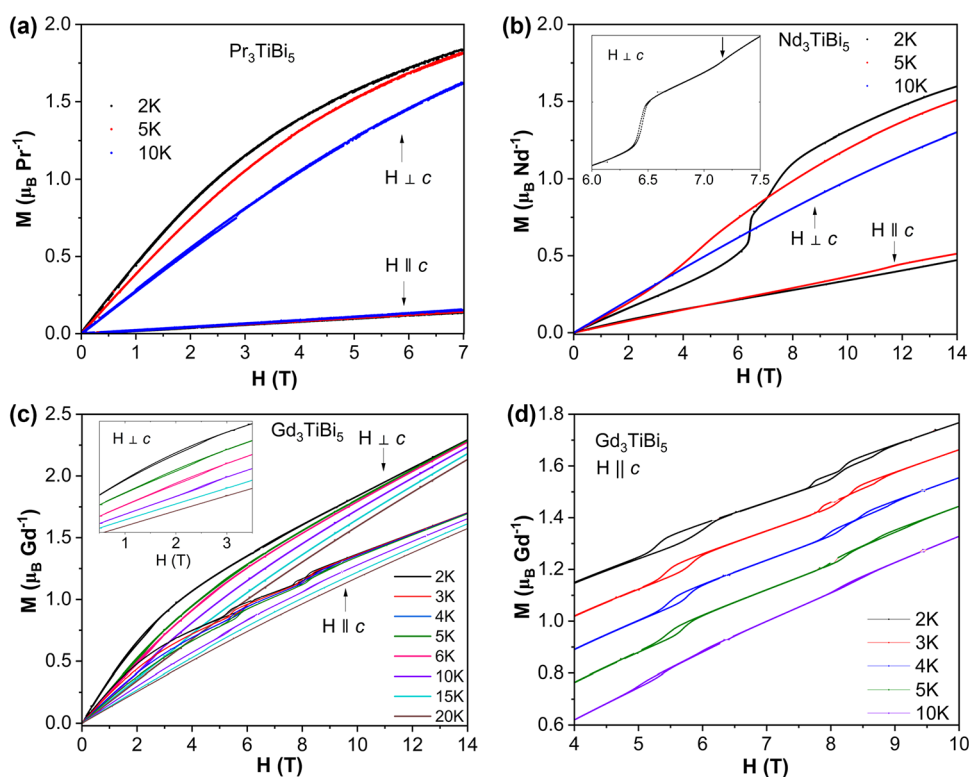


Figure 4. Magnetization vs magnetic field (0–7 T) plots of (a) Pr_3TiBi_5 , (b) Nd_3TiBi_5 , and (c) Gd_3TiBi_5 . Magnetization vs magnetic field (4–10 T) plots of (d) Gd_3TiBi_5 .

strongly bonding with a predominant bonding status below the Fermi level (Figures S7–S9).

Magnetic Properties

The temperature dependence of the magnetic susceptibility and inverse magnetic susceptibility with the magnetic field applied parallel and perpendicular to the c axis of single crystals of Ln_3TiBi_5 ($\text{Ln} = \text{Pr}, \text{Nd}, \text{Gd}$) is shown in Figure 3. Pr_3TiBi_5 shows no magnetic transitions for both field orientations ($H \perp c$ and $H \parallel c$), though we do note there is a broad hump-like feature that can be seen near 30 K (Figure 3a), possibly an indication of a competition between ferromagnetic (FM) and antiferromagnetic (AFM) correlations within the compound. This observation is more pronounced in inverse magnetic susceptibility $1/\chi$ versus temperature plots (Figure 3b). The Curie–Weiss fits of the data from 120 to 300 K yield Curie–Weiss temperatures of $\theta_{C-W,\parallel} = -61.62$ K and $\theta_{C-W,\perp} = 16.17$ K, and effective magnetic moments of $\mu_{\parallel} = 3.27$ and $\mu_{\perp} = 3.41 \mu_B$, when the field is applied parallel and perpendicular to the c axis of the Pr_3TiBi_5 crystal, respectively. The easy axis is in the ab -plane. An average effective magnetic moment that is calculated as $\mu_{av} = (\mu_{\parallel} + 2\mu_{\perp})/3$ is equal to $3.36 \mu_B$, which agrees well with the calculated value of $3.58 \mu_B$ for Pr^{3+} . For Nd_3TiBi_5 , magnetic susceptibility $\chi_{\perp}(T)$ with the magnetic field applied perpendicular to the c axis ($H \perp c$) of the crystal exhibits paramagnetic behavior between 6.3 and 300 K (Figure 3c). The susceptibility peaks at a Néel temperature (T_N) of 6.2 K and drops rapidly at lower temperatures, indicating an antiferromagnetic transition. The $\chi_{\parallel}(T)$ data with the magnetic field applied parallel to the c axis of the crystal ($H \parallel c$) also show an antiferromagnetic ordering at 6.2 K but exhibit an overall lower magnetic susceptibility (Figure 3c). The crystal displays a significant magnetocrystalline anisotropy with $\chi_{\perp}(T_N)/\chi_{\parallel}(T_N) = 3.45$. Curie–Weiss law fits of the inverse magnetic susceptibility

(Figure 3d) perpendicular and parallel to the c axis, $\chi_{\perp}^{-1}(T)$ and $\chi_{\parallel}^{-1}(T)$, from 120 to 300 K result in effective magnetic moments of 3.60 and $3.57 \mu_B$, respectively. The average effective magnetic moment calculated as $\mu_{av} = (\mu_{\parallel} + 2\mu_{\perp})/3$ is equal to $3.59 \mu_B$, agreeing with the calculated μ_{eff} of $3.61 \mu_B$. The Curie–Weiss temperatures from the fits are $\theta_{C-W,\parallel} = -38.13$ K and $\theta_{C-W,\perp} = 4.31$ K. Gd_3TiBi_5 exhibits antiferromagnetic transitions at 17.1 K ($H \parallel c$) and 18.8 K ($H \perp c$) (Figure 3e). The separate ordering temperatures are unexpected given the fact that the crystal structure has one Gd site, suggesting competing ground states for this compound. There is a notable lack of magnetocrystalline anisotropy in Gd_3TiBi_5 . One explanation has to do with spin–orbit coupling (SOC) interactions of the rare-earth ions. In a free-standing Gd^{3+} cation, the total orbital angular momentum is 0. This suggests there should be no magnetic anisotropy between $H \perp c$ and $H \parallel c$ in Gd_3TiBi_5 . Nonetheless, magnetocrystalline anisotropy could result from crystal structure effects given the quasi-1D structure. The heat capacity data shown in Figure 5a for the Gd_3TiBi_5 sample show two clear transitions that coincide with the transition temperatures seen in magnetic susceptibility. This effect could originate from competing ground states near each other in energy, or perhaps from preferential magnetic ordering depending on the applied field orientation. The Curie–Weiss temperatures are $\theta_{C-W,\parallel} = -62.39$ K and $\theta_{C-W,\perp} = -61.29$ K, obtained by fitting the inverse magnetic susceptibility vs temperature plots (Figure 3f) with the Curie–Weiss law from 120 to 300 K. The effective magnetic moments are $\mu_{\parallel} = 8.22$ and $\mu_{\perp} = 8.06 \mu_B$. The average effective magnetic moment calculated as $\mu_{av} = (\mu_{\parallel} + 2\mu_{\perp})/3$ is equal to $8.11 \mu_B$.

Magnetization vs magnetic field plots of Pr_3TiBi_5 show no features within the magnetic fields of 0–7 T and temperatures of 2, 5, and 10 K, though we note that the moment per Pr for $H \perp c$

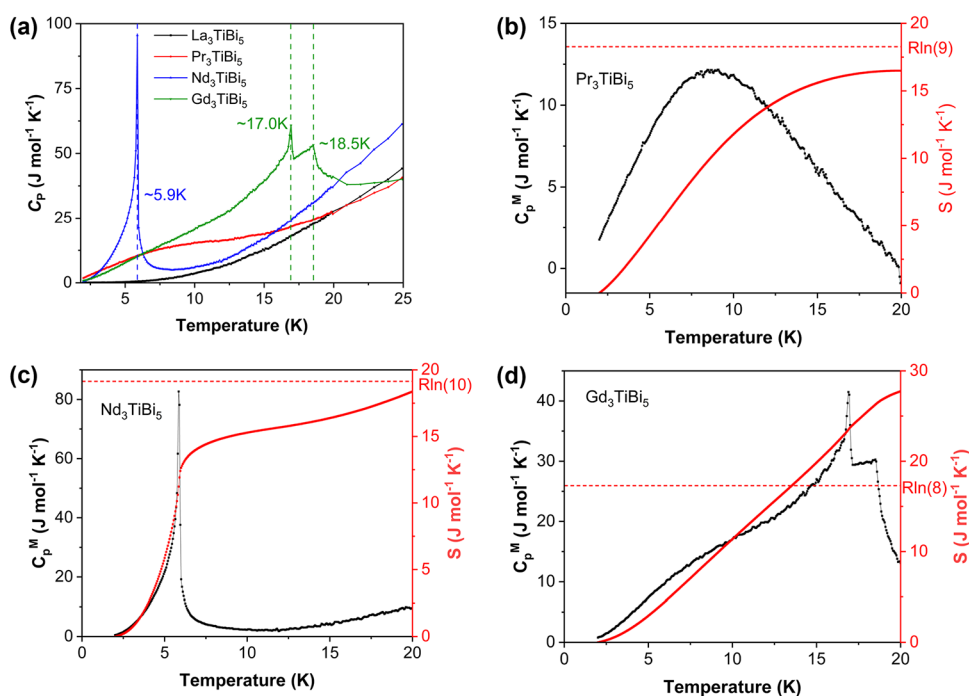


Figure 5. (a) Heat capacity (C_p) of Ln_3TiBi_5 ($\text{Ln} = \text{La}, \text{Pr}, \text{Nd}, \text{Gd}$); magnetic heat capacity and entropy of (b) Pr_3TiBi_5 , (c) Nd_3TiBi_5 , and (d) Gd_3TiBi_5 . Theoretical maximum entropies are shown as dashed red lines calculated by $S_{\text{max}} = R \ln(2J + 1)$. The experimental S_m were obtained by integrating the magnetic heat capacity, which is shown as red solid curves.

does not saturate by 7 T (Figure 4a). The Nd_3TiBi_5 sample shows the presence of a hysteretic metamagnetic transition near 6.2 T ($H \perp c$) at 2 K, as well as another metamagnetic transition indicated by the change in slope near 7.2 T (Figure 4b). A similar change in slope of magnetization can be observed around 11.4 T for $H \parallel c$ at 5 K, which disappears at 2 K (Figure S10). We observe the presence of metamagnetic hysteretic transitions in Gd_3TiBi_5 . For $H \perp c$, these hysteretic loops are observed at 2 K between 1 and 3 T, and with increasing temperature the loops shrink until they can no longer be observed at 15 K (Figure 4c). When the field is applied parallel to the c axis of the crystal, Gd_3TiBi_5 displays metamagnetic transitions near 4–6 T from 2 to 10 K (Figure 4d). Additionally, there are hysteretic metamagnetic transitions between 7.9 and 9 T for $H \parallel c$, which morph into one another at a base temperature of 2 K and proceed to separate and close in the middle as the temperature is increased to 3, 4, and 5 K (Figure 4d). Hints of the lower hysteretic transition persist to 10 K (Figure 4d). The exact nature of these metamagnetic transitions is unclear from these data and warrants further study by diffraction techniques. During the preparation of our revised manuscript, another report on Gd_3TiBi_5 has been published,⁷² and there is overall agreement between magnetic measurements.

The magnetic properties of Ln_3TiBi_5 ($\text{Ln} = \text{Ce}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Gd}$)^{54,55,72} are summarized in Table S4. Ln_3TiBi_5 ($\text{Ln} = \text{Ce}, \text{Nd}, \text{Gd}$) shows antiferromagnetic ordering with transition temperatures of 5.0, 6.2, and 17.1–19 K. Pr_3TiBi_5 shows no magnetic ordering down to 2 K, while Sm_3TiBi_5 shows an anomaly at 14.8 K with an ordering state different from the conventional antiferromagnetic ordering. Since magnetic exchange in these phases is likely mediated by RKKY interactions, we correlated the de Gennes parameters⁷³ for the corresponding lanthanides with magnetic ordering temperatures (Figure S11). While Ln_3TiBi_5 ($\text{Ln} = \text{Ce}, \text{Nd}, \text{Gd}$) ordering temperatures follow a linear trend, Pr_3TiBi_5 unexpectedly lacks magnetic ordering

down to 2 K. On the other hand, the ordering temperature in Sm_3TiBi_5 , 14.8 K, is significantly higher than expected from the linear trend, ~ 8 K. The exact nature of the transition in Sm_3TiBi_5 is unknown and can also be attributed to a structural transition or a valence transition, offering an explanation for such a large deviation from the expected value.

Heat Capacity

Heat capacity (C_p) measurements were performed to further verify the magnetic properties of Ln_3TiBi_5 ($\text{Ln} = \text{Pr}, \text{Nd}$, and Gd). As shown in Figure 5a, Ln_3TiBi_5 ($\text{Ln} = \text{Pr}, \text{Nd}, \text{Gd}$) displays a Schottky-like broad feature from 2 to 25 K, which is likely attributed to crystal electric field splitting effects of the rare-earth ions. Pr_3TiBi_5 shows no transitions, whereas Nd_3TiBi_5 peaks at 5.9 K, consistent with the AFM ordering in the magnetic properties. Two distinct transitions appear at 18.5 and 17.0 K in Gd_3TiBi_5 , matching the AFM ordering identified from magnetic susceptibility data.

To obtain the magnetic heat capacity contribution of Pr, Nd, and Gd, the heat capacity of La_3TiBi_5 was measured and subtracted from that of Ln_3TiBi_5 ($\text{Ln} = \text{Pr}, \text{Nd}, \text{Gd}$) down to a base temperature of 2 K. The resulting magnetic heat capacity C_p^M and entropy S_m are shown in Figure 5b–d. The theoretical maximum entropies of Ln_3TiBi_5 ($\text{Ln} = \text{Pr}, \text{Nd}, \text{Gd}$), shown as dashed red lines, were calculated by $S_{\text{max}} = R \ln(2J + 1)$ where R is the ideal gas constant and J is the total angular momentum quantum number. S_{max} values of Ln_3TiBi_5 ($\text{Ln} = \text{Pr}, \text{Nd}, \text{Gd}$) are 18.27, 19.14, and 17.29 $\text{J mol}^{-1} \text{K}^{-1}$, respectively. The experimental S_m values were obtained by integrating the magnetic heat capacity, which is shown as red solid curves. The experimental S_m values of Pr_3TiBi_5 and Nd_3TiBi_5 are slightly smaller than the theoretical S_{max} value, matching up well with the expectations. The experimental S_m of Gd_3TiBi_5 surpasses the theoretical limit, suggesting that the phonon background for the Gd compound could be more complex than that of the

nonmagnetic La analogue, though the exact nature of the difference is not understood from this study.

CONCLUSIONS

In this report, we have prepared and studied the properties of Ln_3TiBi_5 ($\text{Ln} = \text{Pr}$, Nd , and Gd) hosting 1D Bi chains. DFT calculations studied the topological states of Ln_3TiBi_5 ($\text{Ln} = \text{Pr}$, Nd , Gd), in which band crossing is located above the Fermi level in Pr_3TiBi_5 and Nd_3TiBi_5 , while the band structure of Gd_3TiBi_5 exhibits topologically nontrivial regions near the Fermi level without SOC. Since the band structure of Gd_3TiBi_5 is primarily derived from Bi, SOC has a strong influence on the band structure, inducing a gap for the band crossing along M-K, moving the band crossing along M-K upward away from the Fermi level, shifting degeneracies toward the Fermi level, and flattening the band structure. COHP calculations indicate the bonding status of Ln-Bi_{6g} , Ln-Bi_{4d} , Ti-Bi_{6g} , $\text{Bi}_{4d}\text{-Bi}_{4d}$, and Ti-Ti in Ln_3TiBi_5 ($\text{Ln} = \text{Pr}$, Nd , Gd). The bonding and antibonding status below the Fermi level in 1D Bi chains further demonstrates the formation of hypervalent bonding. Magnetic measurements from single crystals show strong magnetocrystalline anisotropy with an easy axis in the ab -plane for Pr_3TiBi_5 and Nd_3TiBi_5 and a much weaker anisotropy in Gd_3TiBi_5 . Pr_3TiBi_5 does not show any ordering, while Nd_3TiBi_5 and Gd_3TiBi_5 display antiferromagnetic ordering at low temperatures, which was further verified by heat capacity. This work fills the gap in the Ln_3TiBi_5 family by synthesizing Pr_3TiBi_5 and Nd_3TiBi_5 and extends this series to Gd_3TiBi_5 , a promising topological material.

EXPERIMENTAL METHODS

Reagents

Bi (Unique Metals, 99.99%) and Ti (Bean Town Chemical, 99.5%) were used as received. La (Luciteria, 99.5%), Pr (Luciteria, 99.6%), Nd (Luciteria, 99.5%), Sm (Luciteria, 99.95%), and Gd (Luciteria, 99.95%) were arc-melted to remove the oxide layers, followed by storage in a glovebox and cutting into smaller pieces before use in a reaction.

Synthesis

Single crystals of Ln_3TiBi_5 ($\text{Ln} = \text{Pr}$, Nd , and Gd) were grown via Bi flux reaction. For Ln_3TiBi_5 ($\text{Ln} = \text{Pr}$ and Nd), Ln, Ti, and Bi were loaded into alumina crucibles (9 and 6 mm outer and inner diameters, respectively) in the molar ratio of 3:1:45. The crucibles were then loaded into quartz tubes (12 and 10.5 mm outer and inner diameters, 20 cm long). A piece of silica wool was placed above each crucible for product filtration. After that, the tubes were flame-sealed under vacuum and placed into a programmable box furnace. The sealed reactions were heated to 900 °C over 2 h, held there for 8 h, followed by cooling to 500 °C at a rate of 5 °C/h. Upon cooling to 500 °C, the reactions were immediately centrifuged to remove the excess Bi flux. For Gd_3TiBi_5 , Gd, Ti, and Bi were combined in the molar ratio of 3:1:90. The sealed reaction was heated to 750 °C over 2 h, held there for 8 h, followed by cooling to 450 °C at a rate of 5 °C/h. The resulting single crystals are silver-metallic with a rod-like morphology and are air-sensitive. To compare the Bi–Bi bond lengths in Bi–Bi chains of Ln_3TiBi_5 ($\text{Ln} = \text{La}$, Ce , Pr , Nd , Sm , Gd), we synthesized Ce_3TiBi_5 and Sm_3TiBi_5 to get the cif files. For Ce_3TiBi_5 , the synthesis method is similar to that of Pr_3TiBi_5 , except that the molar ratio of Ce, Ti, and Bi is 3:1:60 and the cooling rate from 900 to 500 °C is 100 °C/h. Similarly, Sm_3TiBi_5 is prepared using the Pr_3TiBi_5 procedure except that the reaction was cooled down from 900 to 500 °C in 12 h. To obtain the magnetic heat capacity contribution of Pr, Nd, and Gd, the nonmagnetic La_3TiBi_5 was prepared following the procedure described in ref 53, with a slight change. La, Ti, and Bi with the mass of 0.1, 0.0115, and 3.3 g were combined and reacted at 1000 °C for 6 h followed by cooling to 500 °C in 12 h.

Single-Crystal XRD

Single-crystal XRD experiments (Mo $K\alpha$ radiation) were performed on a Bruker D8 QUEST diffractometer equipped with a PHOTON 100 CMOS area detector at room temperature. Structures of Ln_3TiBi_5 ($\text{Ln} = \text{Pr}$, Nd , and Gd) were solved by the intrinsic phasing method (SHELXT⁷⁴ and Olex2⁷⁵) and refined by the full-matrix least-squares method against F^2 in an anisotropic approximation (SHELXL⁷⁶).

Energy-Dispersive Spectroscopy (EDS)

The compositions of Ln_3TiBi_5 ($\text{Ln} = \text{Pr}$, Nd , Sm , Gd) were confirmed by EDS (Figure S12) performed on a Thermo Fisher Scientific Teneo field-emission scanning electron microscope at the Georgia Electron Microscopy facility.

Calculations

First-principles calculations were performed using density functional theory (DFT) with the Vienna Ab-initio Package (VASP) plane-wave code,^{77,78} generalized gradient approximation of Perdew, Burke, and Ernzerhof (PBE),⁷⁹ and the projector augmented wave (PAW) method.^{80,81} The energy cutoff for the plane-wave expansion was set to 520 eV. The following pseudopotentials are selected for DFT calculations: Pr_3, Nd_3, Gd_3, Bi_d, and Ti_sv. Structure optimization and self-consistent field (SCF) calculations were performed using a Γ -centered $9 \times 9 \times 8$ Monkhorst–Pack mesh. Density of state calculations were done with and without spin–orbit coupling using Γ -centered $15 \times 15 \times 15$ Monkhorst–Pack mesh.⁸² The k -paths for band structure calculations were generated using the VASPKIT package.⁸³ The COHP calculation was done using a Γ -centered $15 \times 15 \times 13$ Monkhorst–Pack mesh.⁸² The COHP analysis is performed by LOBSTER program⁸⁴ with the basis set of VASPPit2015 and charge spilling of 0.87%, 0.92%, and 0.90% for Pr_3TiBi_5 , Nd_3TiBi_5 , and Gd_3TiBi_5 .

Magnetism and Heat Capacity

Temperature- and field-dependent magnetic measurements were carried out with a Quantum Design Magnetic Properties Measurement System (MPMS) and the VSM module of a Quantum Design Dynacool Physical Properties Measurement System (PPMS). $\chi_d(T)$ measurements were conducted in zero-field-cooled (ZFC) and field-cooled (FC) modes. Consecutive $M(H)$ scans at fixed temperatures were started in the ZFC mode by first warming the sample well into the paramagnetic (PM) regime around 100 K, oscillating the field to get rid of any remnant field, and then cooling down to the desired temperatures. All magnetic property measurements were performed on samples mounted on a quartz rod with GE varnish covering the sample to avoid decomposition from exposure to air. Samples were measured with the field along the needles' long axis ($H \parallel c$) and perpendicular to the long axis ($H \perp c$). Heat capacity measurements were carried out with 14 T PPMS and Dynacool PPMS systems. All shown heat capacity measurements were performed at zero applied field.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsmaterialsau.6c00162>.

Crystallographic data, bond lengths of Bi–Bi, M–Bi, Sb–Sb, and M–Sb; summary of magnetic properties of Ln_3TiBi_5 ($\text{Ln} = \text{Ce}$, Pr , Nd , Sm , Gd), band structures of Pr_3TiBi_5 and Nd_3TiBi_5 without SOC, orbital-projected band structures for Gd_3TiBi_5 without SOC, COHP plots for Ln_3TiBi_5 ($\text{Ln} = \text{Pr}$, Nd , Gd), M–H plots of Nd_3TiBi_5 at 2 and 5 K, magnetic transition temperatures vs de Gennes factors in Ln_3TiBi_5 ($\text{Ln} = \text{Ce}$, Nd , Sm , Gd), EDS data of Ln_3TiBi_5 ($\text{Ln} = \text{Pr}$, Nd , Gd) (PDF)

Accession Codes

Deposition Numbers 2564935–2564939 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via the joint Cambridge Crystallographic Data Centre (CCDC) and Fachinformationszentrum Karlsruhe Access Structures service.

AUTHOR INFORMATION

Corresponding Author

Vladislav V. Klepov – Department of Chemistry, University of Georgia, Athens, Georgia 30602, United States; orcid.org/0000-0002-2039-2457; Email: klepov@uga.edu

Authors

Kaige Wu – Department of Chemistry, University of Georgia, Athens, Georgia 30602, United States

Danila S. Sokratov – Maryland Quantum Materials Center and Department of Physics, University of Maryland, College Park, Maryland 20742, United States; orcid.org/0000-0003-0073-4218

Ram Kumar – Maryland Quantum Materials Center and Department of Physics, University of Maryland, College Park, Maryland 20742, United States

Hope A. Long – Department of Chemistry, University of Georgia, Athens, Georgia 30602, United States; orcid.org/0009-0007-4991-1170

Johnpierre Paglione – Maryland Quantum Materials Center and Department of Physics, University of Maryland, College Park, Maryland 20742, United States; Canadian Institute for Advanced Research, Toronto, Ontario M5G 1Z8, Canada

Complete contact information is available at:

<https://pubs.acs.org/10.1021/acsmaterialsau.6c00162>

Author Contributions

[†]K.W. and D.S.S. contributed equally to this paper.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the University of Georgia Department of Chemistry, Franklin College of Arts and Sciences, and the Office of Provost. The computational study was supported in part by resources and technical expertise from the Georgia Advanced Computing Resource Center, a partnership between the University of Georgia's Office of the Vice President for Research and the Office of the Vice President for Information Technology. Research at the University of Maryland was supported by the Gordon and Betty Moore Foundation's EPIQS Initiative Grant No. GBMF9071, the U.S. National Science Foundation Grant No. DMR2303090, and the Maryland Quantum Materials Center.

REFERENCES

- (1) Keimer, B.; Moore, J. The physics of quantum materials. *Nat. Phys.* **2017**, *13* (11), 1045–1055.
- (2) Li, J.; Zhang, Z.; Wang, C.; Huang, H.; Gu, B.-L.; Duan, W. Topological semimetals from the perspective of first-principles calculations. *J. Appl. Phys.* **2020**, *128* (19), No. 191101.
- (3) Liu, H.; Liang, J.; Sun, T.; Wang, L. Recent progress in topological semimetal and its realization in Heusler compounds. *Mater. Today Phys.* **2024**, *41*, No. 101343.
- (4) Lv, B.; Qian, T.; Ding, H. Experimental perspective on three-dimensional topological semimetals. *Rev. Mod. Phys.* **2021**, *93* (2), No. 025002.
- (5) Armitage, N.; Mele, E.; Vishwanath, A. Weyl and Dirac semimetals in three-dimensional solids. *Rev. Mod. Phys.* **2018**, *90* (1), No. 015001.
- (6) Wang, S.; Lin, B.-C.; Wang, A.-Q.; Yu, D.-P.; Liao, Z.-M. Quantum transport in Dirac and Weyl semimetals: a review. *Adv. Phys. X* **2017**, *2* (3), 518–544.
- (7) Burkov, A. A. Topological semimetals. *Nat. Mater.* **2016**, *15* (11), 1145–1148.
- (8) Wang, A.; Baranets, S.; Liu, Y.; Tong, X.; Stavitski, E.; Zhang, J.; Chai, Y.; Yin, W.-G.; Bobev, S.; Petrovic, C. Magnetic mixed valent semimetal EuZnSb₂ with Dirac states in the band structure. *Phys. Rev. Res.* **2020**, *2* (3), No. 033462.
- (9) Schoop, L. M.; Pielnhofer, F.; Lotsch, B. V. Chemical principles of topological semimetals. *Chem. Mater.* **2018**, *30* (10), 3155–3176.
- (10) Yan, B.; Felser, C. Topological materials: Weyl semimetals. *Annu. Rev. Condens. Matter Phys.* **2017**, *8* (1), 337–354.
- (11) Hasan, M. Z.; Xu, S.-Y.; Belopolski, I.; Huang, S.-M. Discovery of Weyl fermion semimetals and topological Fermi arc states. *Annu. Rev. Condens. Matter Phys.* **2017**, *8* (1), 289–309.
- (12) Winkler, G. W.; Singh, S.; Soluyanov, A. A. Topology of triple-point metals. *Chin. Phys. B* **2019**, *28* (7), No. 077303.
- (13) Hirschmann, M. M.; Leonhardt, A.; Kilic, B.; Fabini, D. H.; Snyder, A. P. Symmetry-enforced band crossings in tetragonal materials: Dirac and Weyl degeneracies on points, lines, and planes. *Phys. Rev. Mater.* **2021**, *5* (5), No. 054202.
- (14) Abrashuly, A.; Guo, C.; Papadakis, G. T.; Catrysse, P. B.; Fan, S. Weyl points in a twisted multilayer photonic system. *Appl. Phys. Lett.* **2024**, *125* (17), No. 171703.
- (15) Novoselov, K. S.; Geim, A. K.; Morozov, S. V.; Jiang, D.; Katsnelson, M. I.; Grigorieva, I. V.; Dubonos, S. V.; Firsov, A. A. Two-dimensional gas of massless Dirac fermions in graphene. *Nature* **2005**, *438* (7065), 197–200.
- (16) Shekhar, C.; Nayak, A. K.; Sun, Y.; Schmidt, M.; Nicklas, M.; Leermakers, I.; Zeitler, U.; Skourski, Y.; Wosnitza, J.; Liu, Z.; et al. Extremely large magnetoresistance and ultrahigh mobility in the topological Weyl semimetal candidate NbP. *Nat. Phys.* **2015**, *11* (8), 645–649.
- (17) Neupane, M.; Xu, S.-Y.; Sankar, R.; Alidoust, N.; Bian, G.; Liu, C.; Belopolski, I.; Chang, T.-R.; Jeng, H.-T.; Lin, H.; et al. Observation of a three-dimensional topological Dirac semimetal phase in high-mobility Cd₃As₂. *Nat. Commun.* **2014**, *5* (1), No. 3786.
- (18) Liang, T.; Gibson, Q.; Ali, M. N.; Liu, M.; Cava, R.; Ong, N. Ultrahigh mobility and giant magnetoresistance in the Dirac semimetal Cd₃As₂. *Nat. Mater.* **2015**, *14* (3), 280–284.
- (19) Ali, M. N.; Schoop, L.; Xiong, J.; Flynn, S.; Gibson, Q.; Hirschberger, M.; Ong, N. P.; Cava, R. J. Correlation of crystal quality and extreme magnetoresistance of WTe₂. *Europhys. Lett.* **2015**, *110* (6), No. 67002.
- (20) Zivieri, R.; Lumetti, S.; Létang, J. High-Mobility Topological Semimetals as Novel Materials for Huge Magnetoresistance Effect and New Type of Quantum Hall Effect. *Materials* **2023**, *16* (24), No. 7579.
- (21) Xin, N.; Lourembam, J.; Kumaravadeivel, P.; Kazantsev, A.; Wu, Z.; Mullan, C.; Barrier, J.; Geim, A. A.; Grigorieva, I.; Mishchenko, A.; et al. Giant magnetoresistance of Dirac plasma in high-mobility graphene. *Nature* **2023**, *616* (7956), 270–274.
- (22) Acharya, G.; Pandey, K.; Sharma, M.; Wang, J.; Chhetri, S. K.; Nabi, M. R. U.; Upreti, D.; Basnet, R.; Sakon, J.; Hu, J. Large negative magnetoresistance in the off-stoichiometric topological semimetal PrSb₂Te_{2-x}. *Phys. Rev. B* **2025**, *111* (2), No. 024421.
- (23) Bernevig, B. A.; Hughes, T. L.; Zhang, S.-C. Quantum spin Hall effect and topological phase transition in HgTe quantum wells. *Science* **2006**, *314* (5806), 1757–1761.
- (24) Hu, J.; Xu, S.-Y.; Ni, N.; Mao, Z. Transport of topological semimetals. *Annu. Rev. Mater. Res.* **2019**, *49* (1), 207–252.
- (25) Conte, A. M.; Pulci, O.; Bechstedt, F. Electronic and optical properties of topological semimetal Cd₃As₂. *Sci. Rep.* **2017**, *7* (1), No. 45500.

- (26) Xu, B.; Dai, Y.; Zhao, L.; Wang, K.; Yang, R.; Zhang, W.; Liu, J.; Xiao, H.; Chen, G.; Taylor, A. J.; et al. Optical spectroscopy of the Weyl semimetal TaAs. *Phys. Rev. B* **2016**, *93* (12), No. 121110.
- (27) Schröter, N. B. M.; Stolz, S.; Manna, K.; De Juan, F.; Vergniory, M. G.; Krieger, J. A.; Pei, D.; Schmitt, T.; Dudin, P.; Kim, T. K.; et al. Observation and control of maximal Chern numbers in a chiral topological semimetal. *Science* **2020**, *369* (6500), 179–183.
- (28) Flicker, F.; De Juan, F.; Bradlyn, B.; Morimoto, T.; Vergniory, M. G.; Grushin, A. G. Chiral optical response of multifold fermions. *Phys. Rev. B* **2018**, *98* (15), No. 155145.
- (29) Šmejkal, L.; Jungwirth, T.; Sinova, J. Route towards Dirac and Weyl antiferromagnetic spintronics. *Phys. Status Solidi (RRL)* **2017**, *11* (4), No. 1700044.
- (30) Pesin, D.; MacDonald, A. H. Spintronics and pseudospintronics in graphene and topological insulators. *Nat. Mater.* **2012**, *11* (5), 409–416.
- (31) Wang, L.; Yang, Y.; Wang, J.; Liu, W.; Liu, Y.; Gong, J.; Liu, G.; Wang, X.; Cheng, Z.; Zhang, X. Excellent catalytic performance toward the hydrogen evolution reaction in topological semimetals. *EcoMat* **2023**, *5* (4), No. e12316.
- (32) Rajamathi, C. R.; Gupta, U.; Kumar, N.; Yang, H.; Sun, Y.; Süß, V.; Shekhar, C.; Schmidt, M.; Blumtritt, H.; Werner, P.; et al. Weyl semimetals as hydrogen evolution catalysts. *Adv. Mater.* **2017**, *29* (19), No. 1606202.
- (33) Yang, L.; Wang, D.; Li, J.; Wang, P.; Hou, X.; Tang, K.; Wang, L.; Dong, Z.; Zhang, K. Ternary nodal-line semimetal InNbS₂ for highly sensitive broadband terahertz photodetection. *J. Phys. D Appl. Phys.* **2025**, *58* (6), No. 065107.
- (34) Liu, J.; Xia, F.; Xiao, D.; Garcia de Abajo, F. J.; Sun, D. Semimetals for high-performance photodetection. *Nat. Mater.* **2020**, *19* (8), 830–837.
- (35) Karki Chhetri, S.; Basnet, R.; Wang, J.; Pandey, K.; Acharya, G.; Nabi, M. R. U.; Upreti, D.; Sakon, J.; Mortazavi, M.; Hu, J. Evolution of magnetism in the magnetic topological semimetal NdSb_{1-x}Te_{2-x+δ}. *Phys. Rev. B* **2024**, *109* (18), No. 184429.
- (36) Acharya, S.; Pandey, K.; Basnet, R.; Acharya, G.; Nabi, M. R. U.; Wang, J.; Hu, J. Single crystal growth and characterization of topological semimetal ZrSnTe. *J. Alloys Compd.* **2023**, *968*, No. 171903.
- (37) Pandey, K.; Basnet, R.; Wang, J.; Da, B.; Hu, J. Evolution of electronic and magnetic properties in the topological semimetal SmSb_xTe_{2-x}. *Phys. Rev. B* **2022**, *105* (15), No. 155139.
- (38) Pandey, K.; Mondal, D.; Villanova, J. W.; Roll, J.; Basnet, R.; Wegner, A.; Acharya, G.; Nabi, M. R. U.; Ghosh, B.; Fujii, J.; et al. Magnetic topological semimetal phase with electronic correlation enhancement in SmSbTe. *Adv. Quantum Technol.* **2021**, *4* (10), No. 2100063.
- (39) Weng, H.; Dai, X.; Fang, Z. Topological semimetals predicted from first-principles calculations. *J. Phys.:Condens. Matter* **2016**, *28* (30), No. 303001.
- (40) Gao, H.; Venderbos, J. W.; Kim, Y.; Rappe, A. M. Topological semimetals from first principles. *Annu. Rev. Mater. Res.* **2019**, *49* (1), 153–183.
- (41) Hirayama, M.; Okugawa, R.; Murakami, S. Topological semimetals studied by ab initio calculations. *J. Phys. Soc. Jpn.* **2018**, *87* (4), No. 041002.
- (42) Zhang, H.; Pincelli, T.; Jozwiak, C.; Kondo, T.; Ernstorfer, R.; Sato, T.; Zhou, S. Angle-resolved photoemission spectroscopy. *Nat. Rev. Methods Primers* **2022**, *2* (1), No. 54.
- (43) Tao, D.; Hai-Feng, Y.; Jing, Z.; Yi-Wei, L.; Le-Xian, Y.; Zhong-Kai, L.; Yu-Lin, C. Progress of ARPES study on topological semimetals. *Acta Phys. Sin.* **2019**, *68* (22), No. 227102.
- (44) Liu, Z.; Zhou, B.; Zhang, Y.; Wang, Z.; Weng, H.; Prabhakaran, D.; Mo, S.-K.; Shen, Z.; Fang, Z.; Dai, X.; et al. Discovery of a three-dimensional topological Dirac semimetal Na₃Bi. *Science* **2014**, *343* (6173), 864–867.
- (45) Liu, Z. K.; Jiang, J.; Zhou, B.; Wang, Z.; Zhang, Y.; Weng, H.; Prabhakaran, D.; Mo, S. K.; Peng, H.; Dudin, P.; et al. A stable three-dimensional topological Dirac semimetal Cd₃As₂. *Nat. Mater.* **2014**, *13* (7), 677–681.
- (46) Klemenz, S.; Hay, A. K.; Teicher, S. M.; Topp, A.; Cano, J.; Schoop, L. M. The role of delocalized chemical bonding in square-net-based topological semimetals. *J. Am. Chem. Soc.* **2020**, *142* (13), 6350–6359.
- (47) Khoury, J. F.; Schoop, L. M. Chemical bonds in topological materials. *Trends Chem.* **2021**, *3* (9), 700–715.
- (48) Papoian, A.; Hoffmann, R. Hypervalent bonding in one, two, and three dimensions: Extending the Zintl–Klemm concept to nonclassical electron-rich networks. *Angew. Chem., Int. Ed.* **2000**, *39* (14), 2408–2448.
- (49) Khoury, J. F.; Song, X.; Schoop, L. M. Ln₃MBi₅ (Ln = Pr, Nd, Sm; M = Zr, Hf): Intermetallics with Hypervalent Bismuth Chains. *Z. Anorg. Allg. Chem.* **2022**, *648* (15), No. e202200123.
- (50) Klemenz, S.; Lei, S.; Schoop, L. M. Topological semimetals in square-net materials. *Annu. Rev. Mater. Res.* **2019**, *49* (1), 185–206.
- (51) Khoury, J. F.; Han, B.; Jovanovic, M.; Singha, R.; Song, X.; Queiroz, R.; Ong, N.-P.; Schoop, L. M. A class of magnetic topological material candidates with hypervalent Bi chains. *J. Am. Chem. Soc.* **2022**, *144* (22), 9785–9796.
- (52) Murakami, T.; Yamamoto, T.; Takeiri, F.; Nakano, K.; Kageyama, H. Hypervalent bismuthides La₃MBi₅ (M = Ti, Zr, Hf) and related antimonides: absence of superconductivity. *Inorg. Chem.* **2017**, *56* (9), 5041–5045.
- (53) Ovchinnikov, A.; Bobev, S. Undistorted linear Bi chains with hypervalent bonding in La₃TiBi₅ from single-crystal X-ray diffraction. *Acta Crystallogr., Sect. C: Struct. Chem.* **2018**, *74* (5), 618–622.
- (54) Motoyama, G.; Sezaki, M.; Gouchi, J.; Miyoshi, K.; Nishigori, S.; Mutou, T.; Fujiwara, K.; Uwatoko, Y. Magnetic properties of new antiferromagnetic heavy-fermion compounds, Ce₃TiBi₅ and CeTi₃Bi₄. *Phys. B* **2018**, *536*, 142–144.
- (55) Shinozaki, M.; Tsubouchi, G. M. S. N. M.; Fujiwara, K. M. K.; Manago, M. *Single Crystal Growth and Physical Property Measurements of Sm3TiX5 (X = Bi, Sb)*; International Conference on Strongly Correlated Electron Systems; SCES, 2022.
- (56) Morozkin, A.; Sviridov, I. New ternary CeScSi-type RZrSb compounds (R = Y, Gd–Tm, Lu). *J. Alloys Compd.* **2001**, *320* (1), L1–L2.
- (57) Schellenberg, I.; Eul, M.; Hermes, W.; Pöttgen, R. A ¹²¹Sb and ¹⁵¹Eu Mössbauer spectroscopic investigation of EuMn₂Sb₂, EuZn₂Sb₂, YbMn₂Sb₂, and YbZn₂Sb₂. *Z. Anorg. Allg. Chem.* **2010**, *636*, 85–93.
- (58) Zelinska, O. Y.; Mar, A. Ternary rare-earth manganese bismuthides: structures and physical properties of RE₃MnBi₅ (RE = La–Nd) and Sm₂Mn₃Bi₆. *Inorg. Chem.* **2008**, *47* (1), 297–305.
- (59) Tkachuk, A. V.; Crerar, S. J.; Wu, X.; Muirhead, C. P.; Deakin, L.; Mar, A. Structures and Physical Properties of Ternary Antimonides RE₃MSb₅ (M = Zr, Hf), U₃MSb₅ (M = Zr, Hf, Nb), and YbCrSb₃. *MRS Proc.* **2004**, *848*, 141–148.
- (60) Moore, S. H. D.; Deakin, L.; Ferguson, M. J.; Mar, A. Physical Properties and Bonding in RE₃TiSb₅ (RE = La, Ce, Pr, Nd, Sm). *Chem. Mater.* **2002**, *14* (11), 4867–4873.
- (61) Ferguson, M. J.; Hushagen, R. W.; Mar, A. Crystal structures of La₃ZrSb₅, La₃HfSb₅, and LaCrSb₃. Structural relationships in ternary rare-earth antimonides. *J. Alloys Compd.* **1997**, *249* (1–2), 191–198.
- (62) Bollere, G.; Ferguson, M. J.; Hushagen, R. W.; Mar, A. New ternary rare-earth transition-metal antimonides RE₃MSb₅ (RE = La, Ce, Pr, Nd, Sm; M = Ti, Zr, Hf, Nb). *Chem. Mater.* **1995**, *7* (12), 2229–2231.
- (63) Pöttgen, R. Bismuth as reactive and non-reactive flux medium for the synthesis and crystal growth of intermetallics. *Z. Kristallogr. Cryst. Mater.* **2025**, *240* (5–6), 127–139.
- (64) Saparov, B.; Sefat, A. S. Crystals, magnetic and electronic properties of a new ThCr₂Si₂-type BaMn₂Bi₂ and K-doped compositions. *J. Solid State Chem.* **2013**, *204*, 32–39.
- (65) Baranets, S.; Ovchinnikov, A.; Bobev, S. Structural diversity of the Zintl Pnictides with Rare-earth Metals. In *Handbook on the Physics and Chemistry of Rare Earths*; Elsevier: Amsterdam, 2021; Vol. 60, pp 227–324.
- (66) Ortiz, B. R.; Miao, H.; Parker, D. S.; Yang, F.; Samolyuk, G. D.; Clements, E. M.; Rajapitamahuni, A.; Yilmaz, T.; Vescovo, E.; Yan, J.;

et al. Evolution of highly anisotropic magnetism in the titanium-based kagome metals LnTi_3Bi_4 (Ln : $\text{La}\cdots\text{Gd}^{3+}$, Eu^{2+} , Yb^{2+}). *Chem. Mater.* **2023**, 35 (22), 9756–9773.

(67) Da-Chun, P.; Zhong-Ming, S.; Xiao-Wu, L.; Jiang-Gao, M. Synthesis and crystal structure of La_3ScBi_5 . *Chin. J. Inorg. Chem.* **2006**, 22 (8), 1449–1452.

(68) Gornicka, K.; Ortiz, B. R.; Zhang, H.; Christianson, A. D.; May, A. F. Anisotropic magnetic behavior of Nd_3ScBi_5 and Pr_3ScBi_5 single crystals. *Phys. Rev. Mater.* **2025**, 9 (6), No. 064414.

(69) Pan, D.-C.; Sun, Z.-M.; Mao, J.-G. Synthesis and crystal structures of La_3MgBi_5 and LaLiBi_2 . *J. Solid State Chem.* **2006**, 179 (4), 1016–1021.

(70) Hase, I. Recent Progress in the Theory of Flat Bands and Their Realization. *Condens. Matter* **2025**, 10 (4), No. 64.

(71) Duan, L.; Wang, X.; Zhan, F.; Zhang, J.; Hu, Z.; Zhao, J.; Li, W.; Cao, L.; Deng, Z.; Yu, R.; et al. High-pressure synthesis, crystal structure and physical properties of a new Cr-based arsenide La_3CrAs_5 . *Sci. China Mater.* **2020**, 63 (9), 1750–1758.

(72) Wang, R.; Zhao, Z.; Yi, X.; Zhang, Y.; Zhu, K.; Liu, H.; Lv, S.; Bai, C.; Cao, G.; Bao, L.; et al. Snowflake-like sixfold angle-dependent magnetoresistance in the kagome antiferromagnet Gd_3TiBi_5 . *Phys. Rev. B* **2026**, 114 (3), No. 034417.

(73) Elliott, R. *Magnetic Properties of Rare Earth Metals*; Springer: New York, 1972.

(74) Sheldrick, G. M. SHELXT—Integrated space-group and crystal-structure determination. *Acta Crystallogr., Sect. A: Found. Adv.* **2015**, 71, 3–8.

(75) Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A.; Puschmann, H. OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Crystallogr.* **2009**, 42 (2), 339–341.

(76) Sheldrick, G. M. Crystal structure refinement with SHELXL. *Acta Crystallogr., Sect. C: Struct. Chem.* **2015**, 71, 3–8.

(77) Kresse, G.; Furthmüller, J. Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. *Comput. Mater. Sci.* **1996**, 6 (1), 15–50.

(78) Kresse, G.; Furthmüller, J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Phys. Rev. B* **1996**, 54 (16), No. 11169.

(79) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized gradient approximation made simple. *Phys. Rev. Lett.* **1996**, 77 (18), No. 3865.

(80) Blöchl, P. E. Projector augmented-wave method. *Phys. Rev. B* **1994**, 50 (24), No. 17953.

(81) Kresse, G.; Joubert, D. From ultrasoft pseudopotentials to the projector augmented-wave method. *Phys. Rev. B* **1999**, 59 (3), No. 1758.

(82) Monkhorst, H. J.; Pack, J. D. Special points for Brillouin-zone integrations. *Phys. Rev. B* **1976**, 13 (12), No. 5188.

(83) Wang, V.; Xu, N.; Liu, J.-C.; Tang, G.; Geng, W.-T. VASPKIT: A user-friendly interface analysis using VASP code. *Comput. Phys. Commun.* **2021**, 267, No. 108033.

(84) Maintz, S.; Deringer, V. L.; Tchougréeff, A. L.; Dronskowski, R. LOBSTER: a tool to extract chemical bonding from plane-wave based DFT. *J. Comput. Chem.* **2016**, 37, 1030–1035.