Large unsaturated magnetoresistance and electronic structure studies of single-crystal GdBi

Gourav Dwari¹, Souvik Sasmal¹, Shovan Dan, Bishal Maity, Vikas Saini¹, Ruta Kulkarni,

Soma Banik,^{2,3} Rahul Verma,¹ Bahadur Singh,¹ and Arumugam Thamizhavel ^{1,*}

¹Department of Condensed Matter Physics and Materials Science, Tata Institute of Fundamental Research,

Homi Bhabha Road, Colaba, Mumbai 400005, India

²Accelerator Physics and Synchrotrons Utilization Division, Raja Ramanna Centre for Advanced Technology, Indore 452013, India ³Homi Bhabha National Institute, Training School Complex, Anushakti Nagar, Mumbai 400094, India

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Single crystal of the binary equiatomic compound GdBi crystallizing in the rock-salt-type cubic crystal structure with the space group $Fm\bar{3}m$ has been grown by flux method. The electrical and magnetic measurements have been performed on well-oriented single crystals. The antiferromagnetic ordering of the Gd moments is confirmed at $T_N = 27.5$ K. The magnetization measurement performed at 2 K along the principal crystallographic direction [100] attained a value of $1.3 \mu_B/Gd$ in a field of 7 T, which is about 5 times smaller than its saturation value of $7 \mu_B$. Zero-field electrical resistivity reveals a sudden drop at 27.5 K, suggesting a reduction in the spin disorder scattering due to the antiferromagnetic alignment of the Gd moments. The residual resistivity at 2 K is 390 n Ω cm, suggesting a good quality of the grown crystal. The magnetoresistance attains a value of $10^4\%$ with no signature of saturation, in a field of 14 T at T = 2 K. Shubnikov–de Hass oscillations have been observed in the high field range of the magnetoresistance with three fundamental frequencies corresponding to the extremal areas of the Fermi surface. Our results suggest that the extremely large unsaturated magnetoresistance in this compound is due to near compensation of the charge carriers. We also performed angle-resolved photoelectron spectroscopy measurements with different photon energies and compared our results with the calculated band structure of GdBi.

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I. INTRODUCTION

Generally, rare-earth (R) intermetallic compounds exhibit interesting magnetic properties owing to their localized felectrons [1-3]. After the outburst of topological materials [4–11], many of the rare-earth monobismuthides (RBi) crystallizing in the face-centered cubic NaCl type crystal structure were predicted to be topological semimetal accompanied by nontrivial bulk band inversion and topological surface states [12]. The band topology of these compounds can be tuned by varying the rare-earth element, R. Strong spin-orbit coupling (SOC) in LaBi/LaSb which do not contain f electrons, causes a band inversion and topological surface states [13,14]. If La is replaced by a partially filled *f*-shell rare-earth element, then the time-reversal symmetry breaking is introduced and the magnetic transition occurs at low temperature, which has a significant impact on the magnetotransport [15]. Magnetotransport in RBi compounds show interesting features around the magnetic transition, including extremely large magnetoresistance (XMR). Some reasoning has been given for such an XMR behavior in RBi. The magnetically controlled gap opening leads to metal-insulator transition which is partially dependent on the magnetic element present in RBi; this could cause larger scattering in presence of magnetic field. Second, in nonmagnetic RBi the charge carriers show electron-hole compensation which results in quadratic behavior in magnetoresistance (MR). However, in magnetically ordered compounds, if the MR follow the Kohler's scaling law, then the gap opening may not be the reason for such large MR [16]. As an example, in ErBi the 4f electrons order magnetically and the large MR can be considered due to ultrahigh mobility and near compensation of the charge carriers, whereas in nonmagnetic LaBi and LaSb, the strong spin-orbit coupling caused band inversion and topological surface state and exhibited XMR of the order of 10⁵% [13,14]. The field dependence of the electrical resistivity of these two compounds revealed an upturn and plateau which were observed in several semimetallic compounds and hence led to the construction of a universal triangular phase diagram [13,17]. Several of the RBi compounds like PrBi, SmBi, ErBi, HoBi, etc., also exhibit a large MR [16,18–20]. It is interesting to note that in spite of the increasing f electron count, the XMR is still observed, which reveals that the band structure may remain unchanged due to the highly localized nature of the *f* electrons.

In this work, we present a systematic investigation on the magnetotransport properties and electronic structure of GdBi single crystal. The magnetic measurement depicts a long-range antiferromagnetic ordering of Gd³⁺ moments at $T_N = 27.5$ K. The magnetic ordering is further confirmed from the electrical resistivity and specific heat studies. The electrical resistivity displayed a typical semimetallic character in zero-field measurements. With the application of magnetic field, the resistivity revealed an upturn at low temperature similar to a metal-insulator-like transition. At sufficiently high fields in the range 10–14 T, magnetoresistance shows quantum oscillation that provides an easy way to realize charge

^{*}thamizh@tifr.res.in

carrier properties as an influence of Fermi surface at magnetic state. Bulk and surface band structure have been probed using angle-resolved photoelectron spectroscopy (ARPES) measurements and compared with the first-principles band structure results.

II. EXPERIMENTAL METHODS

Although GdBi melts congruently at 1770°C [21], the high melting temperature precludes its growth by Czochralski method due to the high vapor pressure of Bi at such elevated temperature. Hence, the single crystal of GdBi has been grown by a self-flux method using molten Bi as flux. High-purity Gd ingots (99.9%, Alfa Aesar) and Bi lumps (99.998%, Alpha Aesar) were packed into a baked round-bottomed alumina crucible in the molar ratio of Gd:Bi = 20:80 and sealed under vacuum in a quartz tube. The quartz tube was subsequently placed in a box-type resistive heating furnace and the sample was heated to 1100°C with a heating rate of 50°C/h and held at this temperature for about 12 h for homogenization. Then the furnace was cooled down to 920°C at a rate of 1°C/h followed by 3 days of annealing. We centrifuged the excess Bi-flux at 920 °C in order to avoid the formation of GdBi₂ which crystallizes below 910°C. Cubic single crystals of GdBi with typical dimensions of $\approx 2 \times 2 \times 2 \text{ mm}^3$ were obtained. The compositional analysis of the grown crystals was performed using Energy Dispersive X-ray Spectroscopy (EDX). The phase purity of the crystals was confirmed from x-ray diffraction (XRD) performed in a PANalytical x-ray diffractometer equipped with a monochromatic Cu- K_{α} x-ray source ($\lambda = 1.5406$ Å) and the crystals were oriented along the principal crystallographic direction using Laue diffraction using a polychromatic x-ray source. The crystals were cut into desired shapes using a spark erosion electric discharge machine. Magnetic measurements were performed in a SQUID magnetometer (MPMS, Quantum Design, USA) and the electrical and heat capacity measurements were performed in a physical property measurement system (PPMS, Quantum Design, USA). ARPES and resonant photoemission spectroscopy (RPES) measurements were performed at the undulator based ARPES beamline (ARPES BL-10), Indus-2, India. Atomically clean surface of GdBi single crystal was obtained by cleaving the sample in the vacuum of $\sim 5 \times 10^{-11}$ mbar. All the photoemission measurements were carried out at low temperatures of ~20 K using a SPECS Phoibos 150 electron energy analyzer. The base vacuum during the measurement was $\sim 7 \times 10^{-11}$ mbar. ARPES performed using both the synchrotron radiation hv = 54 eV and He-1 source hv =21.2 eV (SPECS UVS 300). The energy resolution at $h\nu =$ 54 eV is 25 meV and at $h\nu = 21.2$ eV is 20 meV with angular resolution of 0.1°. RPES measurements were performed across the Gd 4d-4f resonance in the energy range between 134 and 159 eV with the energy resolution of 45 meV.

III. RESULTS AND DISCUSSION

A. x-Ray diffraction

The crystal structure of GdBi is shown in Fig. 1(a). A small piece of the as-grown crystal, with the flat plane, was subjected to XRD at 300 K with 2θ scan ranging from 10°



FIG. 1. (a) Crystal structure of GdBi. (b) As-grown single crystal of GdBi. (c) Room temperature XRD pattern of a single crystal of GdBi. [(d) and (e)] Backscattered Laue pattern of GdBi for (100) and (111) planes, respectively.

to 90°, peaks corresponding to (h00) planes (h is an even number) are observed at Bragg angles 28.2° and 58.44°, thus confirming the flat plane of the crystal to be the (100) plane. According to the previous report, GdBi crystallizes in a NaCl-type structure with space group $Fm\bar{3}m$ (No. 225) [22]. The Laue pattern corresponding to the (100) plane is shown Fig. 1(d). Well-defined circular spots together with the fourfold symmetry in the (100) plane ascertained the good quality of a single crystal. The composition of the grown crystal was confirmed from EDX measurement.

B. Magnetic properties

The temperature dependence of magnetic susceptibility $\chi(T)$ measured in an applied magnetic field (B) of 0.1 T, parallel to the [100] direction in the temperature range 2-300 K is shown in Fig. 2(a). At T = 27.5 K a sharp drop in χ confirms the antiferromagnetic ordering. At high temperature χ shows a clear Curie-Weiss behavior and the $\chi(T)$ data follow the Curie-Weiss law, $\chi(T) = C/(T - \theta_p)$, where C is the Curie constant and θ_p is the paramagnetic Weiss temperature. The effective magnetic moment μ_{eff} of Gd³⁺ ions can simply be obtained by the relation $\mu_{\text{eff}} = \sqrt{8C}$. The inverse $\chi(T)$ plot is shown in the inset of Fig. 2(a). The solid line shows the fit to the Curie-Weiss law. From the fitting we obtained $\theta_p = -48.6$ K and the Curie constant C = 8.02 emu/mol. The estimated μ_{eff} from the fitting is 8.0 μ_B /Gd which is nearly equal to the theoretical value of 7.9 μ_B of a free Gd³⁺ ion. The negative value of θ_p confirms the antiferromagnetic correlations.

The isothermal magnetization (*M*) measured at various fixed temperatures is shown in Fig. 2(b). The M(B) curves for $T < T_N$ show a small change of slope at around 1 T, signaling a subtle spin reorientation followed by steady increase without any signature of saturation up to a magnetic field of 7 T. The critical field at which the magnetization attains the saturation value for an antiferromagnet at T = 0 K can be estimated using the mean-field model. The expression for the critical



FIG. 2. (a) Magnetic susceptibility (χ) as function of temperature in a 0.1-T magnetic field and (inset) $\chi^{-1}(T)$ fitted in Curie-Weiss law in paramagnetic region. (b) Field dependence of magnetization at different temperature for field parallel to [100].

field H_c is given by [23]:

$$H_c = \frac{M_s}{\chi(T_{\rm N})},\tag{1}$$

where $M_s = 7 \mu_B/\text{Gd}$ is the saturation magnetization of Gd^{3+} ion and $\chi(T = T_N)$ is obtained from Fig. 2(a). Substituting the value of $\chi(T_N) = 0.09454$ emu/mol = $1.6927 \times 10^{-5} \mu_B \text{ Oe}^{-1} \text{ Gd}^{-1}$, the critical field H_c is estimated as 41 T. This value of H_c is in good agreement with the high field magnetization data, where the M_s is attained at a critical field of $H_c = 42$ T [24].

C. Electrical resistivity and magnetoresistance

The temperature dependence of electrical resistivity $\rho_{xx}(T)$ measured in zero field is shown in the main panel of Fig. 3(a). In the absence of magnetic field, the $\rho_{xx}(T)$ decreases linearly as the temperature is decreased and at $T_{\rm N} = 27.5$ K, a drop in $\rho_{xx}(T)$ is observed due to the reduction in the spin disorder scattering. Below T_N , the resistivity drops rapidly and attains a value of about 390 n Ω cm at 2 K. The residual resistivity ratio of the sample is estimated as 82, suggesting a high quality of the crystal. We have also fitted the electrical resistivity data above the magnetic ordering temperature to the usual Bloch-Grüneissen expression (not shown here for brevity) and obtained a ρ_0 value of about 5 $\mu\Omega$ cm. Such a low value of residual resistivity, before the reduction due to spin disorder scattering, further confirms the high quality of the grown crystal. The zerofield $\rho_{xx}(T)$ data, below T_N was fitted with the power law $\rho_{xx}(T) = \rho_0 + aT^n$, as shown in the inset of Fig. 3(a). The best fit to the data was obtained for n = 1.5, typically for most of the rare-earth compounds the resistivity shows a power-law behavior, due to the *e-e* scattering; however, in the present case the low-*T* resistivity data show a $T^{1.5}$ behavior. According to the spin fluctuation theory by Moriya *et al.* [25], the $T^{1.5}$ dependence is observed in antiferromagnetic materials near a quantum critical point [25,26]. The $T^{1.5}$ behavior in a localized *f* electron system GdBi warrants further investigation.

The $\rho_{xx}(T)$ at various applied magnetic fields is also shown in Fig. 3(a). The overall behavior of $\rho_{xx}(T)$ remains the same in the paramagnetic state in applied magnetic fields. The antiferromagnetic transition at $T_{\rm N} = 27.5$ K remains robust for fields as high as 14 T without any shift which is substantiated with the magnetic susceptibility and heat capacity data as well. However, $\rho_{xx}(T)$ shows an upturn well below T_N for fields greater than 1 T. The upturn increases more rapidly with higher magnetic fields and resembles a metal-to-insulator like transition (MIT). Similar behavior has been observed in other RBi (R = Pr, Ho, Er) compounds [16,18,20]. It is interesting to note that the $\rho_{xx}(T)$ goes through a minimum before the upturn and this minimum shifts to higher temperature as the magnetic field is increased. The magnetic field-driven MIT has been observed in systems like WTe₂, NbP [7,27], and semimetallic compounds like MoSi₂, WSi₂, and WP₂ [17,28,29]. Different mechanisms have been put forward for this type of field-induced MIT and large MR in topological materials. For example, in WTe₂ the XMR is attributed to the perfect electron-hole resonance, while in the case of LaBi and LaSb the large MR is attributed to the orbital texture [13]. All these mechanisms are for nonmagnetic systems. GdBi exhibits an antiferromagnetic transition and, typically, in such kinds of materials the positive MR is attributed to the suppression of the T_N due to applied magnetic fields. However, T_N of GdBi is robust and no change in $T_{\rm N}$ has been observed for fields as high as 14 T. Furthermore, the M(B) data by Li *et al*. [24] have revealed that the magnetization increases linearly and attains the field-induced ferromagnetic state at around 42 T, which suggests the gradual spin reorientation. The scattering due to this staggered moment together with near compensation of charge carriers and a very low residual resistivity (vide infra) results in such a large MR.

To understand the field dependence of the electrical resistivity further, we plotted the normalized temperature dependence of MR measured in different fields from 4 to 14 T in steps of 2 T, as shown in Fig. 3(b). It is interesting to see that the normalized curves fall on to a single curve suggesting the T-dependent normalized MR remains almost the same for all magnetic fields. Hence, it can be said that the low temperature behavior of $\rho_{xx}(T)$ is metallic rather insulating in high magnetic fields [30]. A similar behavior is observed in the magnetically ordered ErBi [16]. The upturn in $\rho_{xx}(T)$ at low temperature can be well described by the Kohler's scaling rule [31-33], according to which the field-dependent MR at different temperature will follow the same functional form MR $\propto f(B\tau)$, where τ is the relaxation time that is inversely proportional to $\rho_0(0, T)$ as long as the scattering mechanisms at different temperatures remain same. Following the Kohler's rule, the resistivity $\rho(B, T)$ of GdBi can be



FIG. 3. (a) Temperature dependence of electrical resistivity of GdBi at different applied magnetic fields; the dotted line corresponds to $T_{\rm N}$; (top inset) fitting of resistivity at 14 T magnetic field with Eq. (2); and (bottom inset) power-law fitting of low temperature resistivity. (b) Temperature dependence of MR normalized with its value at T = 2 K at different magnetic fields. (Inset) MR as function of temperature. (c) Field dependence of MR at various temperatures and (inset) power-law fitting of MR at 2 K. (d) Kohler's scaling of MR at different temperatures.

written as

$$\rho(B,T) = \rho_0(0,T) \bigg\{ 1 + \gamma \bigg[\frac{B}{\rho_0(0,T)} \bigg]^m \bigg\}, \qquad (2)$$

where $\rho_0(0, T)$ is the measured resistivity of GdBi at zero applied magnetic field. A fit of Eq. (2), keeping γ as the only adjustable parameter, with data at 14 T, is shown in the top inset of Fig. 3(a). Value of *m* is kept fixed at 1.7, obtained from power-law fitting of magnetoresistance. Deviation becomes large when the temperature is above the transition temperature T_N , which maybe attributed to the change of scattering mechanism, which limits the use of Kohler's law. The above equation also shines light on the presence of a minimum in resistivity at magnetic field due to the coexistence of $\rho(0, T)$ and inverse of that term in $\rho(B, T)$.

Magnetoresistance of GdBi at different temperature is shown in Fig. 3(c) as a function of magnetic field applied in transverse direction of current. At 2 K, MR reaches 5.1×10^3 % in field 10 T and 10.9×10^3 % in 14 T (not shown here), which is extremely large. The best fit of the MR data at 2 K with power law is shown in the inset of Fig. 3(c) where the obtained exponent value is 1.7. For a perfectly compensated semimetal, one would expect this value to be 2. In this present case the exponent value reveals that the charge carriers are nearly compensated and this has been confirmed from the Hall data (to be discussed below). The value of the exponent decreases as temperature is increased from 2 to 20 K and after that it again increases to 100 K with value 1.8, probably due to change of carrier concentration. To verify the applicability of Eq. (2) to the resistivity data, we performed the Kohler's scaling rule to the field-dependent magnetoresistance, shown in Fig. 3(d), where MR is plotted against (B/ρ_0) at different temperatures, and as can be seen, all MR are collapsing onto a single curve as predicted by the scaling rule. Deviation from a straight line behavior is mainly attributed to the different scattering mechanism in GdBi. This also describes why the fitting shown in the top inset of Fig. 3(a) using Eq. (2) is deviating at temperature above T_N .

We have used Hall resistivity (ρ_{xy}) and linear resistivity (ρ_{xx}) data to estimate the carrier concentration of GdBi. Hall measurements were performed in a five-probe geometry followed by antisymmetrization of the data to minimize the contribution of linear resistivity (ρ_{xx}) . The curved nature of Hall data implies the existence of multiple charge carriers. A two-band model is used here to fit the linear conductivity (σ_{xx}) and hall conductivity (σ_{yx}) . In a semiclassical two-band model, complex conductivity can be written as

$$\sigma = e \left[\frac{n_e \mu_e}{1 + i \mu_e B} + \frac{n_h \mu_h}{1 - i \mu_h B} \right],\tag{3}$$

where *e* is the magnitude of elementary charge and σ_{xx} and σ_{yx} are obtained from the real part and imaginary part of σ ,



FIG. 4. (a) σ_{xx} and σ_{yx} of GdBi as a function of magnetic field. Solid lines show the fit with the two-band model. (b) (Top) Electron and hole density and (bottom) electron and hole mobility at different temperature, obtained from two-band model fitting.

respectively; σ_{xx} and σ_{yx} are calculated from experimental ρ_{xx} and ρ_{xy} using the following relations:

$$\sigma_{xx} = \frac{\rho_{xx}}{\rho_{xx}^2 + \rho_{xy}^2},$$
 (4)

$$\sigma_{yx} = \frac{\rho_{xy}}{\rho_{xx}^2 + \rho_{xy}^2}.$$
 (5)

We simultaneously fitted the σ_{xx} and σ_{yx} data at 2 K to the real and imaginary part of Eq. (3) and the best fit is shown in Fig. 4(a). Calculated values of carrier density and mobility at different temperatures is shown in Fig. 4(b). At 2 K the electron and hole density are estimated as $7.08(8) \times 10^{26} \text{ m}^{-3}$ and $7.30(7) \times 10^{26} \text{ m}^{-3}$ which explains the deviation of MR from quadratic behavior in field. As temperature is increased, we see a crossover in electron and hole density, which is consistent with the observat ion that the exponent value (n)in power-law fitting of MR is increasing towards the value 2 as temperature is increased. The estimated mobility at 2 K is also quite large, reaching 0.91(1) m² V⁻¹ s⁻¹ for electrons and $0.99(1) \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ for holes. These values of carrier concentration and mobility are nearly the same as obtained for ErBi and HoBi compounds [16,20]. The nearly compensated nature of the charge carriers together with relatively high mobility are the reasons for the observed large MR which indicates the possibility of topological states in this system. It is to be mentioned here that we have estimated the carrier concentration from the first principles calculations and obtained the values of $5.92 \times 10^{26} \text{ m}^{-3}$ for electrons and 7.07×10^{26} m⁻³ for holes which are in close agreement with the values obtained from the transport measurements.

D. Shubnikov-de Hass oscillations

We have observed oscillation in MR as shown in Fig. 5(a) when the field is ramped from 11–14 T, for temperatures up to 8 K, beyond which it is not discernible. The background subtracted Shubnikov–de Hass (SdH) oscillation (ΔR_{xx}) is shown in Fig. 5(b). It is quite obvious from the shape of the oscillation that it possesses multiple frequencies corresponding to various extremal areas of the Fermi surface. A fast Fourier transform (FFT) of the oscillation revealed three fundamental frequencies at 461 T (F_{α_1}), 871 T (F_{β}), and 1640 T (F_{α_2}), and two harmonics at 2203 T ($F_{\alpha_1+2\beta}$) and 2562 T ($F_{2\alpha_1+\alpha_2}$)



FIG. 5. (a) SdH oscillation in MR data at 1.8K and (inset) oscillation in expanded view. (b) Oscillating part of electrical resistivity of GdBi as a function of inverted magnetic field, and (inset) fast Fourier transform of oscillating part of electrical resistivity. (c) FFT amplitude at different temperature. (d) Mass plot of different frequencies. The solid lines are the fits to the thermal damping factor of the Lifshitz-Kosevich expression. (e) Dingle plots of different frequencies.

as shown in Fig. 5(c). We have estimated the oscillation frequencies from theoretical calculations using SKEAF code [34] after obtaining the Fermi surface from first-principles calculations [discussed later in Fig. 8(f)]. Two frequencies at 510 T and 1963 T, which are close to the experimental frequencies F_{α_1} and F_{α_2} respectively, represent the electron pocket α , observed at high symmetry point X, whereas the calculated frequency of 902 T which is due to the spherical hole pocket at Γ is matching with the experimental frequency F_{β} .

The extremal cross section area (A_i) of these Fermi pockets are calculated from the Onsager relation: $F_i = (\hbar A_i/2\pi e)$, see Table I. The oscillatory part ΔR_{xx} can be described by Lifshitz-Kosevitch expression [35]. The temperaturedependent amplitude, obtained from FFT of ΔR_{xx} , is shown in Fig. 5(c), which shows the oscillation amplitude of individual frequency decreases with increase in temperature, and it follows thermal damping factor $X/\sinh X$, where $X = (2\pi^2 m_i^* k_B T)/(e\hbar B)$. Here index *i* is a representation of a

Fermi pocket	<i>F</i> (T)	m^* (m_e)	<i>T_D</i> (K)	A (nm ⁻²)	k_F (10 ⁷ cm ⁻¹)	v_F (10 ⁷ cm s)	τ (10 ⁻¹³ s)	$\mu_Q \ (\text{cm}^2 \text{V} \text{s})$
α	461	0.360(3)	6.1(1)	4.40	1.18	3.75	1.98	954.5
	1640	0.72(2)	5.2(4)	15.63	2.23	3.56	2.33	564.1
β	871	0.35(2)	14(4)	8.30	1.62	5.38	0.83	416.3

TABLE I. Parameters estimated from SdH oscillation analysis: m^* , effective mass; T_D , Dingle temperature; A, extremal area of the Fermi surface; k_F , Fermi wave vector; v_F , Fermi velocity; τ , quantum relaxation time; and μ_Q , quantum mobility.

Fermi pocket (α or β) and m_i^* is the effective mass corresponding to the frequency F_i . Figure 5(d) shows mass plot for different frequencies, and the extracted effective masses are given in Table I. The estimated effective mass of carriers are very similar to other rare-earth monopnictides [18,32,36]. Also, the field-induced oscillation amplitude damping follows $\exp[-(2\pi^2 m_i^* k_B T_{D_i})/(e\hbar B)]$, where T_{D_i} is the Dingle temperature related with *i*th pocket, and $\frac{1}{B} = \frac{1}{2}(\frac{1}{B_1} + \frac{1}{B_2})$, where B_1 and B_2 represents the range of applied magnetic field used. As multiple frequencies results in such ΔR_{xx} oscillation, FFT amplitude $(A_{\Delta R})$ of individual frequency in different field segments can give the field-dependent amplitude variation. From the $\ln[A_{\Delta R} \sinh(X)/X]$ vs. 1/B fit, see Fig. 5(e), we obtained the Dingle temperatures (T_D) and calculated the quantum relaxation time $\tau_i (= \hbar/2\pi k_B T_{D_i})$ and quantum mobility $\mu_{O_i}(=e\hbar/2\pi k_B T_{D_i} m_i^*)$ of carriers for different pockets, listed in Table I. From the table it is obvious that the quantum mobility is about an order of magnitude less than that of the transport mobility estimated from the Hall measurements. This is because of the fact that the classical or transport mobility is a macroscopic property that is related to the large angle scattering caused by the charge carriers that move inside the material with the application of an electric potential. On the other hand, the quantum mobility is a microscopic property where the charge carriers move through the material in response to quantum mechanical effects, such as scattering by lattice defects and by phonons. In general, quantum mobility is lower than the transport mobility due to different scattering mechanisms. The large angle scattering affects the classical mobility while both large and small angle scatterings affect the quantum mobility, which leads to smaller a value of quantum mobility. SdH oscillations have been observed for different orientations of the sample with respect to the applied magnetic field as shown in Fig. 6.

E. Specific heat

The heat capacity (C_p) of GdBi single crystal in zero magnetic field in the temperature range 2 to 200 K is shown in the main panel of Fig. 7(a). The sharp λ -shaped peak at 27.5 K is observed, confirming the antiferromagnetic ordering in this compound. The heat capacity attains the value of 49.89 J mol⁻¹ K⁻¹ at 200 K which is the expected Dulong-Petit limiting value of 3nR. The field dependence of heat capacity is shown in the inset of Fig. 7(a). It is evident that the magnetic field does not have any effect on the magnetic ordering. Typically, in antiferromagnetic materials the longrange interaction competes with the applied magnetic field, resulting in the lowering of the ordering temperature. As we have already seen in the M(B) data, the 4f moments align



FIG. 6. (a) SdH oscillations at different angle. (b) Angular dependence of SdH frequencies.



FIG. 7. (a) Specific heat (C_p) of GdBi and LuBi as function of temperature, and (inset) C_p vs. Temperature at different magnetic field. (b) (Top) C_{4f}/T versus temperature and (bottom) magnetic entropy as a function of temperature.



FIG. 8. ARPES results of GdBi measured with (a) synchrotron radiation at photon energies hv = 54 eV and (b) He-1 source hv = 21.2 eV. (c) The zoomed region near the Fermi level ($E_F = 0 \text{ eV}$) measured with He-1 source hv = 21.2 eV. The orbital projected band structure of nonmagnetic GdBi (d) without and (e) with SOC. The Bi p and Gd d orbitals are shown in red and blue, respectively. The Fermi level is with a black dashed line. (f) Fermi surface within the bulk Brillouin zone. The hole and electron pockets are shown in red and blue, respectively.

to the applied field direction in an extremely slow rate and the field-induced ferromagnetic state is achieved at high magnetic field of 42 T [24]. Hence, fields up to 8 T do not have any effect on the heat capacity peak.

Next, we estimate the magnetic contribution $C_{4f}(T)$ to the heat capacity of GdBi, and to accomplish this we have grown the single crystal of LuBi which possesses the same rock-salt-type cubic crystal structure and a completely filled 4f-shell. Due to the difference in atomic mass of Gd and Lu, obtained C_p of LuBi cannot completely mimic the lattice contribution of GdBi. A correction to the C_p is required [37] to obtain the correct value of specific heat. The correction factor in this case is calculated to be 1.02, which is very small and here neglected. After subtracting the lattice and electronic part, the obtained magnetic specific heat of GdBi is shown in Fig. 7(b) (bottom) as C_{4f}/T . A broad hump is observed in the C_{4f}/T plot at the low-temperature region. This type of hump arises for the systems with (2S + 1)-fold degenerate ground state with large S values [38]. For large S the entropy is large, and in order to accommodate the increased entropy a hump appears in the heat capacity. For S = 7/2 systems according to the mean-field theory, the hump in $C_{4f}(T)$ data appears at $T \leq T_{\rm N}/3$ [38]. The hump appears at 9.2 K, which agrees well with the MFT for $T_{\rm N} = 27.5$ K in GdBi. The magnetic entropy S_{4f} attains a value of 13.02 J K⁻¹ mol⁻¹ at T_N , which is 75% of $R\ln(2S+1) = 17.3$ J K⁻¹ mol⁻¹ for S = 7/2. The reduction in the entropy may be attributed to

the inaccurate estimate of the lattice contribution to the heat capacity.

F. Electronic structure studies

ARPES measurements on GdBi single crystal have been performed at hv = 54- and 21.2-eV photon energies to determine the electronic structure. Probing depth at hv = 54 eV [Fig. 8(a)] is ≈ 5 Å while at hv = 21.2 eV [Fig. 8(b)] it is ≈ 10 Å. This implies that bands observed at 21.2-eV photon energy has higher bulk sensitivity than the bands observed at 54-eV photon energy. Photoionization cross section of Gd 5d states is ≈ 2 times higher than the Bi 6p states at both the energies, and hence the observed bands near the Fermi level E_F have dominating Gd 5d character. Comparing Figs. 8(a) and 8(b) we find prominent differences in the bulk and surface band structure. The 54-eV spectrum shows two hole pockets at the Γ point corresponding to the hybridized Gd 5d and Bi 6p states [39] and matches with the band structure reported in the Ref. [12]. Bulk band inversion near the X point is clearly observed in Fig. 8(b) (marked by arrow) while it is absent on the surface in Fig. 8(a). Bulk band inversion is expected to give rise to nontrivial band topology with multiple topological surface states [12,40]. In Fig. 8(c) we find an electron-like band with quite enhanced intensity overlapped on the holelike band at the Γ point. This electron-like band in Fig. 8(c) corresponds to the topological surface state and has also been prominently observed in Fig. 8(a) near E_F . Similar band crossings of electron- and holelike topological states are also observed in PrGe with the onset of the antiferromagnetic phase [41]. The gapless topological surface states in GdBi at the Γ point are predicted in the DFT calculations; however, no clear evidence is observed in Ref. [12].

We also performed electronic structure calculations within the framework of density functional theory framework using the Vienna *ab initio* simulation package (VASP) [42,43]. The generalized gradient approximation [44] was used to include the exchange-correlation effects, and SOC was added self-consistently. We considered the kinetic energy cutoff of 320 eV for the plane-wave basis set and used a Γ -centered $11 \times 11 \times 11 \ k$ mesh for bulk Brillouin zone (BZ) sampling. The Gd *f* electrons were considered as core electrons in our calculations. We generated the Fermi surface by constructing material-specific tight-binding Hamiltonian using the VASP2WANNIER90 interface [45].

The orbital resolved bulk band structure along the high symmetry directions is shown in Figs. 8(d) and 8(e), where red and blue represent Bi p and Gd d orbital characters, respectively. Both the Bi p and Gd d contribute to the states close to the Fermi level. We find three bands along Γ -X line that cross the Fermi level and the band inversion happens between Bi p and Gd d states at the X points, which is consistent with the ARPES measurements shown in Fig. 8(b). The Fermi surface of GdBi is shown in Fig. 8(f). The conical-shaped electron pockets are located at the X points, whereas the spherical and star-shaped hole pockets are centered at Γ in the BZ. The spherical pocket lies inside the star-shaped hole pocket.

To understand the nature of valence states on the surface we have performed the RPES measurement across Gd 4d-4fresonance. Valence band (VB) spectra of GdBi are recorded in the energy range from 135 to 159 eV and are shown in the contour plot in Fig. 9(a). The inelastic background has been subtracted using the Tougaard method [46]. Four prominent features are observed in the VB region at 0.4, 1.5, 5, and 9.35 eV in Fig. 9(a) and are marked as A, B, C, and D respectively. A, B, and C correspond to the hybridized Gd 5d and Bi 6p states while feature D has dominating contribution of Gd 4f states [39]. Bi $5d_{5/2}$ and Bi $5d_{3/2}$ states in Fig. 9(a) are marked as E and F and observed at 24 and 27 eV, respectively. All the valence band spectra are normalized at the Bi 5d peaks (*E* and *F*). The off-resonance spectra at hv = 140 eV and the on-resonance spectra at hv = 150 eV are superimposed on the contour plot in Fig. 9(a). We can see a prominent enhancement in the intensity of feature D at the resonance indicating the binding energy position of the Gd 4 f states \approx 9.35 eV in GdBi. We have also observed a small enhancement in the intensity of the features A, B, and C at the resonance indicating that the Gd 4f states are hybridized with the Gd 5d states.

In the vicinity of the resonance process, constant initial state (CIS) spectra have been shown to give rise to a characteristic Fano line profile [41,47–49] which originates from the interference between direct photoemission and Auger emission like process. The Fano profile is expressed as $\sigma(h\nu) = \sigma_a \frac{(q+\epsilon)^2}{1+\epsilon^2} + \sigma_b$, where $\epsilon = (h\nu - E_0)/G$. In this expression E_0 is the resonance energy, *G* is the natural width given by the decay rate of the autoionization, and *q* gives the information about the discrete/continuum mixing strength. The cross



FIG. 9. RPES of GdBi showing the contour plot in (a). Blue shows the maximum intensity in the contour plot. The on-resonance spectra at 150 eV and the off-resonance spectra at 140 eV are superimposed on the contour plot and the VB features are marked in (a). CIS spectra for the VB features at different binding energy position (E_B) are plotted in (b) to (f). The solid red dots are the experimental data while the solid blue lines are the fitted Fano profile (discussed in the text in detail). The calculated Fano parameters q, G, and E_0 are also mentioned in (b) to (f).

sections σ_a and σ_b represent the nonresonant background cross sections for transitions to continuum states that interact or do not interact, respectively, with the discrete autoionization states [48]. CIS spectra for the topological surface state are shown in Fig. 9(b) and the valence band features are shown in Figs. 9(c) to 9(f). The CIS intensity plots are obtained from Fig. 9(a) by plotting the normalized intensity at constant binding energy position. The solid lines in Figs. 9(b) to 9(f) are the fitted Fano line shapes with the parameters q, G, and E_0 mentioned in the figures. The value of q for all the features is found to be >2, indicating that all the VB features are localized in nature but the localization is found to be the largest near E_F [$q \approx 5.38$ at $E_B = 0.2$ eV in Fig. 9(b)] for the topological surface state which clearly indicates distinct surface electronic properties than the bulk. The Gd 4f states [feature C and D in Figs. 9(e) and 9(f)] shows a lower value of $q ~(\approx 2)$ than the topological surface states indicating that the 4f states are strongly hybridized with the Gd 5d states. The reason for increase in the localization of the valence states as the energy position is moved closer to E_F [see Figs. 9(b) to 9(f)] is because of the strong hybridization between the Gd 4f and Gd 5d states which causes the empty Gd 4f states to move more into the low-density-state region near the bottom of the conduction band [50].

IV. CONCLUSION

High-quality single crystal of GdBi has been grown by high-temperature solution growth. We have performed a

systematic study on the magnetic and electrical transport properties. From the SdH quantum oscillations, we have analyzed the Fermi surface properties. The magnetic measurements revealed that GdBi undergoes an antiferromagnetic transition at 27.5 K. The isothermal magnetization M(B) does not show any signatures of saturation and reaches a value of $\sim 1.3 \,\mu_{\text{B}}/\text{Gd}$ at 7 T, whereas the saturation moment is 7 μ_{B}/Gd . The electrical resistivity confirms the antiferromagnetic ordering by displaying a drop in the resistivity at 27.5 K and the overall resistivity behavior is typical metallic like. With the application of magnetic field, the electrical resistivity displays a huge upturn in the magnetically ordered state at low temperatures, as observed in most of the compensated semimetallic systems. The MR also displays a large value of the order of 10⁴% without any signature of saturation. Hall effect studies reveal multiple types of charge carriers and near compensation. From SdH oscillation studies, we have estimated the effective mass of carriers corresponding to three fundamental frequencies, which matches with the previously reported other rare-earth monopnictides. ARPES results indicate distinct bulk and surface states present in this system while RPES

- K. H. J. Buschow, Intermetallic compounds of rare-earth and 3d transition metals, Rep. Prog. Phys. 40, 1179 (1977).
- [2] M. O. Ogunbunmi, S. Baranets, and S. Bobev, Synthesis and transport properties of the family of Zintl phases Ca₃RESb₃ (RE = La-Nd, Sm, Gd-Tm, Lu): Exploring the roles of crystallographic disorder and core 4f electrons for enhancing thermoelectric performance, Chem. Mater. **33**, 9382 (2021).
- [3] *Handbook of Magnetic Materials*, edited by K. H. J. Buschow (Elsevier, Amsterdam, 1993).
- [4] M. G. Vergniory, L. Elcoro, C. Felser, N. Regnault, B. A. Bernevig, and Z. Wang, A complete catalogue of high-quality topological materials, Nature (London) 566, 480 (2019).
- [5] S.-M. Huang, S.-Y. Xu, I. Belopolski, C.-C. Lee, G. Chang, B. Wang, N. Alidoust, G. Bian, M. Neupane, C. Zhang, S. Jia, A. Bansil, H. Lin, and M. Z. Hasan, A Weyl Fermion semimetal with surface Fermi arcs in the transition metal monopnictide TaAs class, Nat. Commun. 6, 7373 (2015).
- [6] S.-Y. Xu, I. Belopolski, D. S. Sanchez, C. Zhang, G. Chang, C. Guo, G. Bian, Z. Yuan, H. Lu, T.-R. Chang, P. P. Shibayev, M. L. Prokopovych, N. Alidoust, H. Zheng, C.-C. Lee, S.-M. Huang, R. Sankar, F. Chou, C.-H. Hsu, H.-T. Jeng *et al.*, Experimental discovery of a topological Weyl semimetal state in TaP, Sci. Adv. 1, e1501092 (2015).
- [7] C. Shekhar, A. K. Nayak, Y. Sun, M. Schmidt, M. Nicklas, I. Leermakers, U. Zeitler, Y. Skourski, J. Wosnitza, Z. Liu *et al.*, Extremely large magnetoresistance and ultrahigh mobility in the topological Weyl semimetal candidate NbP, Nat. Phys. 11, 645 (2015).
- [8] S.-Y. Xu, N. Alidoust, I. Belopolski, Z. Yuan, G. Bian, T.-R. Chang, H. Zheng, V. N. Strocov, D. S. Sanchez, G. Chang, C. Zhang, D. Mou, Y. Wu, L. Huang, C.-C. Lee, S.-M. Huang, B. Wang, A. Bansil, H.-T. Jeng, T. Neupert *et al.*, Discovery of a Weyl fermion state with Fermi arcs in niobium arsenide, Nat. Phys. **11**, 748 (2015).

results indicate that the surface state near E_F has more localized character. Hence, the compensated nature of the charge carriers observed in resistivity is governed by the localized character of surface states. Moreover, the high mobility of the conduction electrons is due to the spin polarized Gd 5*d* states which are strongly hybridized with the Gd 4*f* states. A high field MR measurements at low temperatures and fields greater than 14 T will throw more light on the observed nonsaturating magnetoresistance.

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- [9] Z. K. Liu, B. Zhou, Y. Zhang, Z. J. Wang, H. M. Weng, D. Prabhakaran, S.-K. Mo, Z. X. Shen, Z. Fang, X. Dai, Z. Hussain, and Y. L. Chen, Discovery of a three-dimensional topological Dirac semimetal, Na₃Bi, Science **343**, 864 (2014).
- [10] S. Borisenko, Q. Gibson, D. Evtushinsky, V. Zabolotnyy, B. Büchner, and R. J. Cava, Experimental Realization of a Three-Dimensional Dirac Semimetal, Phys. Rev. Lett. **113**, 027603 (2014).
- [11] P. Gebauer, H. Poddig, L. T. Corredor-Bohorquez, T. V. Menshchikova, I. P. Rusinov, P. Golub, F. Caglieris, C. Benndorf, T. Lindemann, E. V. Chulkov, A. U. B. Wolter, B. Büchner, T. Doert, and A. Isaeva, Heavy-atom antiferromagnet GdBiTe: An interplay of magnetism and topology in a symmetry-protected topological semimetal, Chem. Mater. 33, 2420 (2021).
- [12] P. Li, Z. Wu, F. Wu, C. Cao, C. Guo, Y. Wu, Y. Liu, Z. Sun, C.-M. Cheng, D.-S. Lin, F. Steglich, H. Yuan, T.-C. Chiang, and Y. Liu, Tunable electronic structure and surface states in rare-earth monobismuthides with partially filled *f* shell, Phys. Rev. B **98**, 085103 (2018).
- [13] F. Fallah Tafti, Q. Gibson, S. Kushwaha, J. W. Krizan, N. Haldolaarachchige, and R. J. Cava, Temperature-field phase diagram of extreme magnetoresistance, Proc. Natl. Acad. Sci. USA 113, E3475 (2016).
- [14] F. F. Tafti, Q. D. Gibson, S. K. Kushwaha, N. Haldolaarachchige, and R. J. Cava, Resistivity plateau and extreme magnetoresistance in LaSb, Nat. Phys. 12, 272 (2016).
- [15] B. Kuthanazhi, N. H. Jo, L. Xiang, S. L. Bud'ko, and P. C. Canfield, Magnetisation and magneto-transport measurements on CeBi single crystals, Philos. Mag. **102**, 542 (2022).
- [16] L.-Y. Fan, F. Tang, W. Z. Meng, W. Zhao, L. Zhang, Z. D. Han, B. Qian, X.-F. Jiang, X. M. Zhang, and Y. Fang, Anisotropic and extreme magnetoresistance in the magnetic semimetal

candidate erbium monobismuthide, Phys. Rev. B **102**, 104417 (2020).

- [17] R. Mondal, S. Sasmal, R. Kulkarni, A. Maurya, A. Nakamura, D. Aoki, H. Harima, and A. Thamizhavel, Extremely large magnetoresistance, anisotropic Hall effect, and Fermi surface topology in single-crystalline WSi₂, Phys. Rev. B **102**, 115158 (2020).
- [18] A. Vashist, R. K. Gopal, D. Srivastava, M. Karppinen, and Y. Singh, Fermi surface topology and large magnetoresistance in the topological semimetal candidate PrBi, Phys. Rev. B 99, 245131 (2019).
- [19] A. P. Sakhya, P. L. Paulose, A. Thamizhavel, and K. Maiti, Evidence of nontrivial Berry phase and Kondo physics in SmBi, Phys. Rev. Mater. 5, 054201 (2021).
- [20] Z. M. Wu, Y. R. Ruan, F. Tang, L. Zhang, Y. Fang, J.-M. Zhang, Z. D. Han, R. J. Tang, B. Qian, and X. F. Jiang, Multiple metamagnetism, extreme magnetoresistance and nontrivial topological electronic structures in the magnetic semimetal candidate holmium monobismuthide, New J. Phys. 21, 093063 (2019).
- [21] R. J. Gambino, Rare-earth-Sb and -Bi compounds with the Gd₄Bi₃ (anti-Th₃P₄) structure, J. Less-Common Met. **12**, 344 (1967).
- [22] K. Yoshihara, J. Taylor, L. Calvert, and J. Despault, Rare-earth bismuthides, J. Less-Common Met. 41, 329 (1975).
- [23] V. K. Anand and D. C. Johnston, Physical properties of EuPd₂As₂ single crystals, J. Phys.: Condens. Matter 26, 286002 (2014).
- [24] D. X. Li, Y. Haga, H. Shida, T. Suzuki, Y. S. Kwon, and G. Kido, Magnetic properties of stoichiometric Gd monopnictides, J. Phys.: Condens. Matter 9, 10777 (1997).
- [25] T. Moriya and T. Takimoto, Anomalous properties around magnetic instability in heavy electron systems, J. Phys. Soc. Jpn. 64, 960 (1995).
- [26] S. Julian, F. Carter, F. Grosche, R. Haselwimmer, S. Lister, N. Mathur, G. McMullan, C. Pfleiderer, S. Saxena, I. Walker, N. Wilson, and G. Lonzarich, Non-Fermi-liquid behaviour in magnetic d- and f-electron systems, J. Magn. Magn. Mater. 177-181, 265 (1998).
- [27] M. N. Ali, J. Xiong, S. Flynn, J. Tao, Q. D. Gibson, L. M. Schoop, T. Liang, N. Haldolaarachchige, M. Hirschberger, N. P. Ong, and R. J. Cava, Large, non-saturating magnetoresistance in WTe₂, Nature (London) **514**, 205 (2014).
- [28] M. Matin, R. Mondal, N. Barman, A. Thamizhavel, and S. K. Dhar, Extremely large magnetoresistance induced by Zeeman effect-driven electron-hole compensation and topological protection in MoSi₂, Phys. Rev. B **97**, 205130 (2018).
- [29] N. Kumar, Y. Sun, N. Xu, K. Manna, M. Yao, V. Süss, I. Leermakers, O. Young, T. Förster, M. Schmidt, H. Borrmann, B. Yan, U. Zeitler, M. Shi, C. Felser, and C. Shekhar, Extremely high magnetoresistance and conductivity in the type-II Weyl semimetals WP₂ and MoP₂, Nat. Commun. 8, 1642 (2017).
- [30] L. R. Thoutam, Y. L. Wang, Z. L. Xiao, S. Das, A. Luican-Mayer, R. Divan, G. W. Crabtree, and W. K. Kwok, Temperature-Dependent Three-Dimensional Anisotropy of the Magnetoresistance in WTe₂, Phys. Rev. Lett. **115**, 046602 (2015).
- [31] Y. L. Wang, L. R. Thoutam, Z. L. Xiao, J. Hu, S. Das, Z. Q. Mao, J. Wei, R. Divan, A. Luican-Mayer, G. W. Crabtree, and

W. K. Kwok, Origin of the turn-on temperature behavior in WTe₂, Phys. Rev. B **92**, 180402(R) (2015).

- [32] O. Pavlosiuk, P. Swatek, D. Kaczorowski, and P. Wiśniewski, Magnetoresistance in LuBi and YBi semimetals due to nearly perfect carrier compensation, Phys. Rev. B 97, 235132 (2018).
- [33] J. Du, Z. Lou, S. N. Zhang, Y. Zhou, B. Xu, Q. Chen, Y. Tang, S. Chen, H. Chen, Q. Zhu, H. Wang, J. Yang, Q. S. Wu, O. V. Yazyev, and M. Fang, Extremely large magnetoresistance in the topologically trivial semimetal α – WP₂, Phys. Rev. B 97, 245101 (2018).
- [34] P. Rourke and S. Julian, Numerical extraction of de Haas-van Alphen frequencies from calculated band energies, Comput. Phys. Commun. 183, 324 (2012).
- [35] D. Shoenberg, *Magnetic Oscillations in Metals* (Cambridge University Press, Cambridge, UK, 2009).
- [36] L. Ye, T. Suzuki, C. R. Wicker, and J. G. Checkelsky, Extreme magnetoresistance in magnetic rare-earth monopnictides, Phys. Rev. B 97, 081108(R) (2018).
- [37] M. Bouvier, P. Lethuillier, and D. Schmitt, Specific heat in some gadolinium compounds. I. Experimental, Phys. Rev. B 43, 13137 (1991).
- [38] D. C. Johnston, R. J. McQueeney, B. Lake, A. Honecker, M. E. Zhitomirsky, R. Nath, Y. Furukawa, V. P. Antropov, and Y. Singh, Magnetic exchange interactions in BaMn₂As₂: A case study of the J₁-J₂-J_c Heisenberg model, Phys. Rev. B 84, 094445 (2011).
- [39] R. Masrour, E. Hlil, M. Hamedoun, and A. Benyoussef, Investigation of electronic and magnetic properties of antiferromagnetic GdBi system by first principle and series expansions calculations, Comput. Mater. Sci. 84, 45 (2014).
- [40] J. Nayak, S.-C. Wu, N. Kumar, C. Shekhar, S. Singh, J. Fink, E. E. D. Rienks, G. H. Fecher, S. S. P. Parkin, B. Yan, and C. Felser, Multiple Dirac cones at the surface of the topological metal LaBi, Nat. Commun. 8, 13942 (2017).
- [41] S. Banik, P. K. Das, A. Bendounan, I. Vobornik, A. Arya, N. Beaulieu, J. Fujii, A. Thamizhavel, P. U. Sastry, A. K. Sinha, D. M. Phase, and S. K. Deb, Giant Rashba effect at the topological surface of PrGe revealing antiferromagnetic spintronics, Sci. Rep. 7, 4120 (2017).
- [42] W. Kohn and L. J. Sham, Self-consistent equations including exchange and correlation effects, Phys. Rev. 140, A1133 (1965).
- [43] G. Kresse and D. Joubert, From ultrasoft pseudopotentials to the projector augmented-wave method, Phys. Rev. B 59, 1758 (1999).
- [44] J. P. Perdew, K. Burke, and M. Ernzerhof, Generalized Gradient Approximation Made Simple, Phys. Rev. Lett. 77, 3865 (1996).
- [45] A. A. Mostofi, J. R. Yates, Y.-S. Lee, I. Souza, D. Vanderbilt, and N. Marzari, wannier90: A tool for obtaining maximallylocalised Wannier functions, Comput. Phys. Commun. 178, 685 (2008).
- [46] S. Tougaard, Practical algorithm for background subtraction, Surf. Sci. 216, 343 (1989).
- [47] U. Fano, Effects of configuration interaction on intensities and phase shifts, Phys. Rev. 124, 1866 (1961).
- [48] S. Banik, A. Bendounan, A. Thamizhavel, A. Arya, P. Risterucci, F. Sirotti, A. K. Sinha, S. K. Dhar, and S. K. Deb, Electronic structure of EuCu₂Ge₂ studied by resonant photoemission and x-ray absorption spectroscopy, Phys. Rev. B 86, 085134 (2012).

- [49] S. Banik, M. K. Chattopadhyay, S. Tripathi, R. Rawat, and S. N. Jha, Large positive magnetoresistance and Dzyaloshinskii-Moriya interaction in CrSi driven by Cr 3d localization, Sci. Rep. 10, 12030 (2020).
- [50] P. Larson and W. R. L. Lambrecht, Electronic structure of Gd pnictides calculated within the LSDA + U approach, Phys. Rev. B 74, 085108 (2006).