Magnetic mixed valent semimetal EuZnSb$_2$ with Dirac states in the band structure

Aifeng Wang (王爱峰)1,4,4 Sviantoslav Baranets2, Yu Liu (刘育)1,4 Xiao Tong4, E. Stavitski,4 Jing Zhang,5 Yisheng Chai,5 Wei-Guo Yin (尹卫国)1,3,§ Svilen Bobev2,1 and C. Petrovic1,**

1Condensed Matter Physics and Materials Science Department, Brookhaven National Laboratory, Upton, New York 11973, USA
2Department of Chemistry and Biochemistry, University of Delaware, Newark, Delaware 19716, USA
3Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, New York 11973, USA
4National Synchrotron Light Source II, Brookhaven National Laboratory, Upton, New York 11973, USA
5Low Temperature Physics Laboratory, College of Physics, Chongqing University, Chongqing 401331, China

(Received 3 May 2020; accepted 5 August 2020; published 22 September 2020)

We report discovery of antiferromagnetic semimetal EuZnSb$_2$, obtained and studied in the form of single crystals. Electric resistivity, magnetic susceptibility, and heat capacity indicate antiferromagnetic order of Eu with $T_N = 20$ K. The effective moment of Eu$^{3+}$ inferred from the magnetization and specific heat measurement is 3.5 $\mu_B$, smaller than the theoretical value of Eu$^{2+}$ due to presence of both Eu$^{3+}$ and Eu$^{2+}$. Magnetic-field-dependent resistivity measurements suggest dominant quasi-two-dimensional Fermi surfaces whereas the first-principle calculations point to the presence of Dirac fermions. Therefore, EuZnSb$_2$ could represent the first platform to study the interplay of dynamical charge fluctuations, localized magnetic 4$f$ moments, and Dirac states with Sb orbital character.

DOI: 10.1103/PhysRevResearch.2.033462

I. INTRODUCTION

Dirac crystals have attracted great attention in recent years [1]. Topological semimetals with linear energy dispersion in momentum space host variety of quantum transport properties, such as the quantum Hall effect (QHE), extremely large magnetoresistance (MR), and high mobility [2–4]. In particular, manipulation of topologically protected Dirac states by antiferromagnetic (AFM) spins in crystals not only gives rise to rich quantum effects but also enables stable devices that dissipate less energy when compared to traditional FM heterostructures [5–7].

In contrast to local-moment compounds with $f$-electron levels deep below Fermi energy or heavy fermions that feature magnetic spin exchange with conduction electron bands, mixed, i.e., noninteger chemical valence (MV) on 4$f$ or 5$f$ electronic orbitals facilitates charge transfer and absence of long-range magnetic order [8,9]. Charge fluctuations exert considerable influence on the conduction electron bands in general and in particular on the formation of Dirac states at topological Kondo insulator surfaces [10–13]. On the other hand, magnetic MV compounds with Dirac topological states are hitherto unknown.

Here we report discovery of a material, EuZnSb$_2$, with 4$f$ magnetic order below $T_N = 20$ K. Magnetic moment of Eu is estimated to be 3.5 $\mu_B$, smaller to that of 7.9 $\mu_B$ in EuMnBi$_2$ due to the presence of MV Eu$^{2+}$ and Eu$^{3+}$ atoms, similar to SmB$_6$ [13]. Angular- and temperature-dependent magnetoresistance (MR) are consistent with a quasi-two-dimensional Fermi surface. First-principles calculations reveal that square lattice Sb 5$p_z$/5$p_y$-derived bands have a Dirac point between $\Gamma$ and $M$ points in the Brillouin zone. This indicates both the topological electronic bands and magnetic texture. Such arrangement in a tunable $ABX_2$ ($A =$ alkaline earth metal and/or rare earth metal, $B =$ transition metal) crystallographic structure where graphene-like two-dimensional (2D) quantum charge transport and high mobility were found [14–20] that can lead to the emergence of rich quantum phases [5,21].

II. EXPERIMENTAL AND THEORETICAL METHODS

Single crystals of EuZnSb$_2$ were grown by the Bridgeman method. First, Eu chunks, Zn particles, and Sb lumps were mixed in a stoichiometric ratio, placed into alumina crucible, and then sealed in a fused silica tube. The quartz tube was slowly heated to 1030 °C. After 2 h, the sample was quickly cooled in 4 h to 850 °C and then slowly cooled to 400 °C at a rate of 3 °C/h. Finally, the quartz tube was cooled to room temperature with the furnace power shut off. Single crystals with size up to $4 \times 2 \times 0.5$ mm$^3$ can be cleaved from the melted ingot.

Magnetotransport and heat capacity measurement up to 9 T were measured in a Quantum Design PPMS-9 instrument. Resistivity $\rho_{xx}$ was measured by a standard four-probe...
method. Hall resistivity $\rho_{xy}$ was measured by the four-terminal technique by switching the polarity of the magnetic field to eliminate the contribution of $\rho_{xx}$.

Powder x-ray diffraction (XRD) data were taken with Cu Kα ($\lambda = 0.15418$ nm) radiation of Rigaku MiniFlex powder diffractometer. The element analysis was performed using an energy-dispersive x-ray spectroscopy (EDX) in a JEOL JSM-6500 scanning electron microscope, confirming stoichiometric EuZnSb$_2$. The x-ray absorption spectroscopy measurement was performed at 8-ID beamline of NSLS II Brookhaven National Laboratory (BNL). The x-ray absorption near edge structure (XANES) and the extended x-ray absorption fine structure (EXAFS) spectra were processed using the Athena software package. The extracted EXAFS signal, $\chi(k)$, was weighed by $k^2$ to emphasize the high-energy oscillation and then Fourier transformed in a $k$ range from 2 to 11 Å$^{-1}$ to analyze the data in the $R$ space.

X-ray photoemission spectroscopy (XPS) experiments were carried out in an ultrahigh vacuum (UHV) system with base pressures less than $2 \times 10^{-9}$ Torr equipped a hemispherical electron energy analyzer (SPECS, PHOIBOS 100) and twin anode x-ray source (SPECS, XR50). Al Kα (1486.7 eV) radiation was used at 10 kV and 30 mA. The angle between the analyzer and x-ray source was 45° and photoelectrons were collected along the sample surface normal.

For accurate crystal structure determination, single-crystal intensity data sets were collected at 200 K in Bruker SMART APEX II CCD diffractometer using graphite monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å). Approximately a quarter sphere of reciprocal space data was collected in two batch runs at different $\omega$ and $\phi$ angles with an exposure time of 6 s/frame. A total of 1415 reflections ($2\theta_{\text{max}} \approx 56^\circ$) were collected, 191 of which were unique ($T_{\text{min}}/T_{\text{max}} = 0.170/0.327$, $R_{\text{int}} = 0.066$). The data collection, data reduction and integration, and refinement of the cell parameters were carried out using the Bruker-provided programs with applied semiempirical absorption correction [22,23]. The structure was subsequently solved by direct methods and refined on $F^2$ (12 parameters) with the aid of the SHELXL package [24]. All atoms were refined with anisotropic displacement parameters with scattering factors (neutral atoms) and absorption coefficients [25]. The final Fourier map is featureless with the highest residual density and deepest hole and absorption coefficients [25]. The final Fourier map is featureless with the highest residual density and deepest hole and absorption coefficients [25]. The final Fourier map is featureless with the highest residual density and deepest hole and absorption coefficients [25]. The final Fourier map is featureless with the highest residual density and deepest hole and absorption coefficients [25]. The final Fourier map is featureless with the highest residual density and deepest hole and absorption coefficients [25]. The final Fourier map is featureless with the highest residual density and deepest hole and absorption coefficients [25]. The final Fourier map is featureless with the highest residual density and deepest hole and absorption coefficients [25]. The final Fourier map is featureless with the highest residual density and deepest hole and absorption coefficients [25]. The final Fourier map is featureless with the highest residual density and deepest hole and absorption coefficients [25]. The final Fourier map is featureless with the highest residual density and deepest hole and absorption coefficients [25].

For first-principles band-structure calculations, we applied the WIEN2k [26] implementation of the full potential linearized augmented plane wave method in the generalized gradient approximation (GGA) [27] + $U_{\text{eff}} = 6$ eV on the Eu 4$f$ orbitals [28–30] with the spin-orbit (SO) coupling treated in the second variation method. The basis size was determined by $R_{\text{int}}R_{\text{max}} = 7$ and the Brillouin zone was sampled with a regular $18 \times 18 \times 3$ mesh containing 162 irreducible $k$ points.

![Crystal Structure of EuZnSb$_2$](image)

**FIG. 1.** (a) Crystal structure of EuZnSb$_2$ projected approximately along [100] with anisotropic displacement parameters drawn at the 90% probability level and with unit cell outlined. Eu atoms are depicted as red crosses, ellipsoids, Zn atoms are shown with blue ellipsoids, and the Sb1 and Sb2 are shown with yellow ellipsoids, respectively. (b) Top view of the Sb square nets. EXAFS oscillation with the model fit (c), Fourier transform magnitudes (d), and a close view of the Eu coordination polyhedron (e) at the room temperature. (f) Powder x-ray diffraction pattern of EuZnSb$_2$ confirms phase purity; vertical tick marks denote reflections in the $P4_2/mnm$ space group. Inset in panel (f) shows average crystal size on a mm scale. (g) Temperature-dependent magnetic susceptibility taken in a 1 T magnetic field both in the zero field cooling and field cooling scale. (h) XPS core-level spectra of Eu (3$d$) in EuZnSb$_2$.

III. RESULTS AND DISCUSSIONS

The EuZnSb$_2$ refined structure [Figs. 1(a) and 1(b)], Tables I and II is ZrCuSiAs-type, Pearson index $P4_212$. EuZnSb$_2$ is a ternary compound in the Eu-Zn-Sb phase diagram. The other known ternary compounds are Eu$_2$ZnSb$_2$, Eu$_2$ZnSb$_2$, Eu$_2$Zn$_4$Sb$_{18}$, and Eu$_{11}$Zn$_6$Sb$_{12}$ [31–34]. EuZnSb$_2$
TABLE I. Selected single-crystal data collection and structure refinement parameters for EuZnSb2 measured at 200 K using $\lambda = 0.71073\ \text{Å}$. The corresponding crystallographic information file (CIF) has been deposited with the Cambridge Crystallographic Data Centre (CCDC), depository no. 1999191.

| Refined composition | EuZnSb2 | Formula mass (g/mol) | 460.83 |
|---------------------|---------|-----------------------|--------|
| Space group         | P4/nmm (no. 129) | Z | 2 |
| a (Å)               | 4.392(4) |
| c (Å)               | 11.21(2) |
| V (Å$^3$)           | 216.2(5) |
| Density (g/cm$^3$)  | 7.08 |
| $R_1 \{I > 2\sigma(I)\}^a$ | 0.058 |
| $wR_2 \{I > 2\sigma(I)\}^a$ | 0.129 |
| $\Delta \rho_{\text{max/min}}/\rho \cdot \text{Å}^{-3}$ | 3.39, 3.96 |

$^aR_1 = \Sigma |F_i| - |F_i|/\Sigma |F_i|, wR2 = (\Sigma (wF^2_0 - |F_i|)^2)/\Sigma (wF^2_0)^2)^{1/2}, w = 1/[σ^2 F^2_0 + (0.0714P)^2 + (0.9825P)], P = (F^2_0 + 2F^2_i)/3.$

TABLE II. Selected single-crystal data collection and structure refinement parameters for EuZnSb2 measured at 200 K using $\lambda = 0.71073\ \text{Å}$.

| Atom | Site | x | y | z | $U_{eq}$ |
|------|------|---|---|---|--------|
| Eu1  | 2c   | 1/4 | 1/4 | 0.2673(2) | 0.015(1) |
| Zn1  | 2a   | 3/4 | 1/4 | 0 | 0.020(1) |
| Sb1  | 2c   | 1/4 | 1/4 | 0.8479(3) | 0.017(1) |
| Sb2  | 2b   | 3/4 | 1/4 | 1/2 | 0.018(1) |

Selected interatomic distances (Å)

|          |          |          |          |          |          |
|----------|----------|----------|----------|----------|----------|
| Zn1−Sb1 | 2.779(3) | Eu1−Sb1 | 3.363(3) |          |          |
| Sb2−Sb2 | 3.105(4) | −Sb2×4  | 3.409(4) |          |          |

The structure prototype is known and will not be described at length. Results of structural refinement are shown in Table I. There are four independent sites in the asymmetric unit (Table II) and based on the refinements, the structure appears to be devoid of disorder on any of them. The nearly spherical shape of the anisotropic displacement parameters is also a testament to this conjecture. The structure is based on PbO-type layers made up of fused ZnSb$_4$ tetrahedra and square nets of Sb atoms [Figs. 1(a) and 1(b)]. All Zn-Sb interatomic distances are within the common range (Table II) and within the range for the sum of the single-bonded covalent radii. The Zn-Sb-Sb angles within the ZnSb$_4$ tetrahedra deviate from the ideal 109.5° value and range from 104.4(2)° to 112.1(1)°. There are no indications from the structure refinements that the Sb square lattice is a subject to a Peierls distortion. The Sb-Sb interatomic distances within the square nets are longer than what is expected for a single covalent Sb-Sb bond, but the atomic interactions in such topology are hypervalent, consistent with the longer distances [3.105(3) Å].

We note that ABX$_2$ (A = alkaline earth metal and/or rare earth metal, B = transition metal) materials feature tunable crystal structures. The square Bi or Sb slabs host graphene-like Dirac states of X = Bi/Sb orbital character with charge-or spin-density wave order coupled to topological states [39–43]. Weyl states were proposed in Sr$_1$xMn$_{1−x}$Sb$_2$ [44,45]. Topological Dirac states were also found in Zn-based 112 materials such as BaZnSb$_2$ and SrZnSb$_2$ [46,47]; EuMnBi$_2$ hosts QHE with field-tunable Eu 4f magnetic order and magnetopiezoelectric effect [48,49].

Figures 1(c) and 1(d) show the Zn K-edge oscillations and corresponding Fourier transform magnitudes of extended x-ray absorption fine structure (EXAFS) spectra of EuZnSb$_2$, respectively. In the single-scattering approximation, the EXAFS could be described by the following equation [50]:

$$\chi(k) = \sum_i N_i S^2_i kR_i^2 f_i(k, R_i) e^{-2R_i/\lambda} e^{-2k^2\sigma^2_i} \sin[2kR_i + \delta_i(k)],$$

where $N_i$ is the number of neighboring atoms at a distance $R_i$ from the photoabsorbing atom, $S^2_i$ is the passive electrons reduction factor, $f_i(k, R_i)$ is the backscattering amplitude, $\lambda$ is the photoelectron mean free path, $\delta_i$ is the phase shift of the photoelectrons, and $\sigma^2_i$ is the correlated Debye-Waller factor measuring the mean square relative displacement of the photoabsorber-backscatter pairs. The corrected main peak around $R \approx 2.77\ \text{Å}$ in Fig. 1(d) corresponds to the Zn-Sb1 bond distances in ZnSb$_4$ tetrahedra and is in good agreement with single-crystal refinement result (Table II). The Eu atoms are coordinated by eight nearest neighbor antimony atoms in a square-antiprismatic fashion [Fig. 1(e)] with Eu-Sb1 and Eu-Sb2 distances longer than 3.3 Å (Table II). Unit cell from the powder x-ray diffraction experiment on pulverized crystals [Fig. 1(f)] can be fitted well with the P4/nmm structural model (Table I), confirming the single-crystal refinement result and phase purity.

Temperature dependence of magnetic susceptibility measured with zero field cooling and field cooling mode is shown in Fig. 1(g) for two primary crystallographic directions. A sharp peak at 20 K was observed for the magnetic susceptibility with H//a, while a saturation behavior is observed...
below 20 K with $H//c$, indicating that the magnetic easy axis is along the $a$ axis. The peak at 20 K can be explained by the antiferromagnetic transition of Eu$^{2+}$. Magnetic susceptibility above 20 K exhibits a typical Curie-Weiss behavior, which can be well fitted to $\chi = \chi_0 + \frac{C}{T - \theta}$, where $\chi_0$ is the temperature-independent Pauli contribution and $C$ is related to the effective moments. The effective moment of Eu$^{2+}$ is 3.5 $\mu_B$ and $\theta = -9.4$ K for $H//ab$ while 3.7 $\mu_B$ and $\theta = -11.2$ K for $H//c$. Negative Curie temperatures indicate dominant antiferromagnetic interactions of Eu$^{2+}$. In order to obtain more information about the magnetic structure of Eu$^{2+}$, we perform the field-dependent measurement of magnetization loop, as shown in the inset in Fig. 1(g). The magnetization along the $c$ axis exhibits perfect linear behavior at 2 and 30 K, i.e., at temperatures below and above $T_N$. When field is applied along the $ab$ plane, the magnetization shows linear behavior in 30 K whereas a very small deviation from linearity is observed at 1.1 T in $M(H)$ taken at 2 K. The temperature and field dependence magnetization of EuZnSb$_2$ [Fig. 1(g)] resembles that of EuZnBi$_2$ whose magnetic structure is analogous to EuMnBi$_2$ spin-flop AFM phase [36,49]. However, these Bi-based materials belong to $14/mmm$ space group containing different Eu-sublattice structure and fixed Eu valence when compared to EuZnSb$_2$. The weak in-plane anisotropy of Eu$^{2+}$ gives rise to the kinks around 1.1 T. For EuZnSb$_2$ the M versus H do not saturate up to 9 T, and no spin flop is observed, in contrast to that in EuZnBi$_2$ [51]. Thus, the magnetic field that might induce the spin flop of Eu$^{2+}$ can be higher than 20 T [49].

X-ray photoelectron 3d core level spectra [Fig. 1(h)] shows spin-orbit split states $3d_{x^2-y^2}$, $3d_{3z^2}$, $3d_{x^2}$, and $3d_{3z^2}$, at binding energies 1125, 1155, 1135, and 1165 eV, respectively, confirming the presence of both Eu$^{2+}$ and Eu$^{3+}$. We also observe a weak satellite peak at somewhat higher binding energies from $3d_{3z^2}$, originating from the multielectronic excitations in the photoelectron emission. The XPS spectrum is rather similar to that of Eu$_2$SrBi$_2$S$_4$F$_4$ [52] and provides explanation for the observed paramagnetic Curie-Weiss moment reduced from 7.9 $\mu_B$. Interestingly, both Eu$^{2+}$ and Eu$^{3+}$ share the same 2c atomic site in the $P4/nmm$ unit cell; this might reduce Zn vacancies when compared to La$_{1-x}$ZnSb$_2$ [53]. The absence of Zn defects and mixed valent Eu suggest that the square-planar nets in EuZnSb$_2$ cannot be treated as hypervalent Sb since for trivalent rare-earth-metal defects on the Zn site are necessary to lower the valence electron count [53,54].

Temperature dependence of the specific heat of EuZnSb$_2$ is shown in Fig. 2(a). The anomaly corresponding to the AFM transition of Eu$^{2+}$ is observed below 20 K [Fig. 2(a) inset]. The anomaly is suppressed to low temperature by magnetic field, consistent with resistivity and magnetization measurement. Room-temperature heat capacity is close to 3N$R$, where $N$ is the atomic number per chemical formula and $R$ is the universal gas constant 8.314 J mol$^{-1}$ K$^{-1}$. Specific heat above 25 K is well fitted by the Debye-Einstein model [55]:

$$C_{el+ph}(T) = \gamma T + a 9nR \left(\frac{T}{\theta_D}\right)^3 \int_0^{\theta_B/T} \frac{x^4 e^x}{(e^{x/T} - 1)^2} dx + (1 - \alpha) 3nR \left(\frac{\theta_B}{T}\right)^2 e^{\theta_B/T} (e^{\theta_B/T} - 1)^{-1} T,$$

where $\theta_D$ and $\theta_B$ are the Debye and Einstein temperatures, respectively, and $\alpha$ denotes the relative contribution of Debye and Einstein terms to phonon heat capacity. The $\theta_D = 233$ K and $\theta_B = 73$ K can be obtained from the fitting. We note that inclusion of the Einstein term was necessary to fit $C(T)$, suggesting the presence of optical phonon modes [56,57]. The entropy change induced by the AFM transition of Eu$^{2+}$ is obtained by $\Delta S = S(C_T - C_{ph+el})/T dT$, and $\Delta S$ is estimated to be 11 J mol$^{-1}$ K$^{-1}$, smaller than the theoretical value $\Delta S = R \ln(2J + 1) = 17.3$ J mol$^{-1}$ K$^{-1}$ for Eu$^{2+}$ with $J = \frac{3}{2}$. However, we can infer $J = 1.38$ from $\Delta S = 11$ J mol$^{-1}$ K$^{-1}$. Then, the effective moment of Eu$^{2+}$ is estimated to be 3.6, in agreement with the magnetization measurement and also with XPS investigation that reveals the presence of both Eu$^{2+}$ and Eu$^{3+}$.

Hall resistivity $\rho_{xy}$ exhibits positive slope and small temperature dependence [Fig. 2(b)], suggesting dominant hole carriers. Clear nonlinear behavior at high field indicates multiband transport, similar to YbMnSb$_2$ [58]. We fit $\rho_{xy}$ with semiclassical two-band model [59]:

$$\rho_{xy} = \frac{B}{e} \left( \frac{n_e \mu_e^2}{n_h \mu_h^2} + \frac{n_h - n_e}{(n_e - n_h)(\mu_h \mu_e)} B^2 \right),$$

where $n_e$ and $\mu_e$ (and $n_h$ and $\mu_h$) denote the carrier concentrations and mobilities of electrons and holes, respectively. The obtained carrier concentration and mobility are shown in
Data were measured at 2 K and the current was always perpendicular to the magnetic field.

The exchange interactions among magnetic moments are five different magnetic structures [Figs. 4(a)–4(e), Table III]. These numbers indicate the mechanism of Dirac point formation and point to possible magnetic easy axis after comparing the total energy for five different magnetic structures [Figs. 4(a)–4(c), Table III].

FIG. 3. (a) Temperature dependence of the in-plane resistivity of EuZnSb$_2$ in 0 and 9 T, respectively. (b) Angle $\theta$ dependence of resistivity at 2 and 30 K, respectively measured in 9 T. (c), (d) Magnetoresistance of EuZnSb$_2$ for $\theta = 0$. Green lines show fits using two-band orbital magnetoresistance obtained using carrier concentrations and mobilities from Figs. 2(c) and 2(d); we note that such fits are possible for carrier concentration and mobility variations for up to $\pm10\%$ and $\pm20\%$ from values reported in Fig. 2. (e) Magnetoresistance at different tilt angles $\theta$ between $B$ and $c$ axis. Data were measured at 2 K and the current was always perpendicular to the magnetic field.

Strong external magnetic MR features $B^2$ dependence in the low field and a saturating MR in high fields [63]. Crossover magnetic field $B^*$ above which the quantum limit is satisfied at specific temperature $T = B^* = (E_F + k_BT)^2
\[ \frac{1}{2\mu} \]$
[67]$ could then be used to estimate Fermi velocity. Such analysis, assuming quantum limit, gives the Fermi velocity $v_F \sim 5.13 \times 10^5$ m s$^{-1}$, i.e., $\Delta_{LL} = 5$ meV. We estimate Fermi energy from $E_F = \hbar^2/m_0(3\pi^2 n)^{2/3}$, where $n$ is the carrier density. By taking measured carrier density [Fig. 2(c)], we obtain $E_F = 16.5$ meV for electron pocket and $E_F = 250$ meV for the hole pocket, suggesting that MR arises from the first few Landau levels. Indeed, the two-band orbital magnetoresistance MR [68]

\[ MR = \frac{n_e \mu_e \mu_s (\mu_e + \mu_s)^2 (\mu_s H)^2}{(\mu_e n_h + \mu_s n_e)^2 + (\mu_s H)^2} \left( n_s - n_e \right) \]

is satisfactory only at high temperatures [Fig. 3(c)].

Other possible reasons for linear MR in high fields include mobility fluctuations in an inhomogeneous crystal [69] or open orbits. The former can be excluded since EuZnSb$_2$ is stoichiometric crystal. The latter usually arises for electronic motion on orbits associated with magnetic field oriented along elongated necks of the Fermi surface, for example, in Cu [70], in topological materials with extremely large magnetoresistance with compensated charge carriers [71] or in two-dimensional conductors where magnetic field is applied parallel to the conducting layers [72]. Whereas we note that EuZnSb$_2$ is not a compensated metal with equal electron and hole concentration [Fig. 2(e)], and that in Figs. 3(c) and 3(d) magnetic field is oriented orthogonal to the quasi-2D conduction direction, we cannot exclude the possibility for open Fermi surface pockets. It also should be noted that small negative MR appears when magnetic field $B$ is tilted away from the $c$ axis at 2 K [Fig. 2(d)]. This likely arises due to in-plane spin reorientation which could indicate shift of the magnetic easy axis with external field rotation.

First-principles band structure calculations reveal the mechanism of Dirac point formation and point to possible magnetic structure after comparing the total energy for five different magnetic structures [Figs. 4(a)–4(c), Table III]. The exchange interactions $J_{SO}S^2 = -1.810(-1.616)$ meV (antiferromagnetic), $J_{SO}S^2 = 1.544(1.558)$ meV, and $JS^2 = 0.856(0.663)$ meV are estimated from GGA with (without) inclusion of spin-orbit coupling [see Figs. 4(a) and 4(c) for the definition of the exchange paths]. These numbers indicate that the AAF3 pattern is the ground state. Figure 4(e) shows the low-energy magnetic structure with the in-plane easy axis obtained by GGA+$U$+SO calculations with $U = 6$ eV for...
FIG. 4. [(a)–(e)] The antiferromagnetic structures used in the first-principles total energy calculations. (f) The electronic band structure calculated with the AAF3-x structure (e) in GGA + U + SO. Red thick circles denote the 5px/5py band derived from the Sb2 square lattices. (g) The calculated Fermi surface of EuZnSb2. Warm colors denote hole carriers and cold colors denote electrons. Electron-like bands are located near the Γ point and X point; hole bands are along the (0,0)–(π,π) line excluding the Γ point states. the Eu 4f orbitals. However, the state is almost degenerate with the one with the out-of-plane easy axis, meaning that the magnetic anisotropy is very weak. The moments of Eu2+ feature ferromagnetic arrangement in plane and are stacked antiferromagnetic by every two layers in the out-plane direction. In its corresponding electronic structure [Fig. 4(f)], the flat bands lying about 1.3 eV below the Fermi level are derived from the Eu 4f orbital. They are moved down from about 200 meV below the Fermi level in GGA calculations by inclusion of U, a feature that is more severe in the DFT calculations for Eu3+N [29] but nearly absent for Eu2+ chalcogenides [28], suggesting that the Eu ionicity in EuZnSb2 be in between EuN and EuO. The square-lattice Sb 5px/5py derived bands have a Dirac point between the Γ and M points, indicating that the system contains both the topological electronic bands and the magnetic texture. The Fermi surface [Fig. 4(g)] shows a coronavirus-like electron pocket at the Γ point surrounded by four hole pockets. The Dirac states around (π/2, π/2) are flat along the c axis; i.e., they are restricted to the Sb2 square lattice. Overall, the volume of the hole pockets are larger than the electron pocket, in agreement with the experiments. The structure at the Γ point features elongated necks which could contribute to open orbits and linear MR, as discussed above. The antiferromagnetic J_{Sb2} (i.e., the exchange interaction between two nearest Eu ions above and below the square-lattice Sb2 layer) means that the time-reversal symmetry is not broken for the itinerant electrons on the Sb2 layers at the level of the mean-field-like calculations, leading to the fourfold-degenerate Dirac states. Yet, it would have been broken by the random distribution of Eu2+ and Eu3+ ions on the same crystal site—leading to the formation of Weyl states—which cannot be described by standard DFT calculations with the 1×1×2 minimal structure model. Further studies of topological electronic structure and putative Weyl states in EuZnSb2 using angular resolved photoemission (ARPES) and large-supercell DFT calculations are of high interest.

IV. CONCLUSION

In conclusion, we report discovery of EuZnSb2, a magnetic semimetal. EuZnSb2 exhibits MV Eu; i.e., both Eu2+ and Eu3+ are present in the unit cell. The Eu2+ moments order antiferromagnetically below 20 K. First-principle calculations are consistent with the presence of Dirac states in the band structure whereas magnetotransport suggests dominant quasi-2D Fermi surface sheets. Further ARPES and neutron experiments are of interest to shed more light on Dirac dispersion in momentum space and magnetic space group in

| Pattern     | GGA   | GGA+SO | GGA+U+SO |
|-------------|-------|--------|----------|
| AAF         | 0     | 0      |          |
| GAF         | 2.88  | 4.49   |          |
| FM          | 1.13  | −0.53  |          |
| AAF2        | 6.46  | 7.24   |          |
| AAF3-x      | −6.23 | −6.18  | 0        |
| AAF3-z      | −2.85 | −0.04  |          |

*a*Magnetization along the z axis.

*b*Magnetization along the x axis.

TABLE III. The first-principles total energy per formula unit of five different magnetic patterns as shown in Fig. 4. FM denotes the ferromagnetic configuration.
the ordered state. Moreover, spectroscopic studies are of interest to investigate possible coupling of dynamical charge fluctuations and the long-range magnetic order with Dirac bands.

ACKNOWLEDGMENTS

Work at Brookhaven is supported by the U.S. DOE under Contract No. DE-SC0012704. Cryogenic magnetization measurements at Chongqing were supported by Fundamental Research Funds for the Central Universities (2018CDJDM04) and Projects of President Foundation of Chongqing University (2019CDXZWL002). Single-crystal diffraction carried out at the University of Delaware was supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, under Award No. DE-SC0008885. This research used resources of the Center for Functional Nanomaterials, which is a U.S. DOE Office of Science Facility, at Brookhaven National Laboratory under Contract No. DE-SC0012704.

[1] T. O. Wehling, A. M. Black-Schaffer, and A. V. Balatsky, Adv. Phys. 63, 1 (2014).
[2] K.-Y. Yang, Y.-M. Lu, and Y. Ran, Phys. Rev. B 84, 075129 (2011).
[3] C. Shekhar, A. K. Nayak, Y. Sun, M. Schmidt, M. Nicklas, I. Leermakers, U. Zeitler, Y. Skouroski, J. Wosnitza, Z. Liu, Y. Chen, W. Schnelle, H. Bormann, Y. Grin, C. Felser, and B. Yan, Nat. Phys. 11, 645 (2015).
[4] Z. Wang, Y. Zheng, Z. Shen, Y. Lu, H. Fang, F. Sheng, Y. Zhou, X. Yang, Y. Li, C. Feng, and Z.-A. Xu, Phys. Rev. B 93, 121112(R) (2016).
[5] L. Smejkal, Y. Mokrousov, B. Yan, and A. H. MacDonald, Nat. Phys. 14, 242 (2018).
[6] D.-F. Shao, G. Gurung, S.-H. Zhang, and E. Y. Tsymbal, Phys. Rev. Lett. 112, 077203 (2014).
[7] D. Zhang, M. Shi, T. Zhu, D. Xing, H. Zhang, and J. Wang, Phys. Rev. Lett. 122, 206401 (2019).
[8] P. Coleman, in Handbook of Magnetism and Advanced Magnetic Materials, edited by H. Kronmüller and S. Parkin (John Wiley & Sons, New York, 2007), Vol. 1, pp. 95–148.
[9] Z. Fisk and J. D. Thompson, Curr. Opin. Solid State Mater. Sci. 21, 42 (1996).
[10] M. Dzero, K. Sun, V. Galitski, and P. Coleman, Phys. Rev. Lett. 104, 106408 (2010).
[11] L. Smejkal, Y. Mokrousov, B. Yan, and A. H. MacDonald, Phys. Rev. Lett. 110, 096401 (2013).
[12] X. Deng, K. Haule, and G. Kotliar, Phys. Rev. Lett. 111, 176404 (2013).
[13] C.-H. Min, P. Lutz, S. Fiedler, B. Y. Kang, B. K. Cho, H.-D. Kim, H. Bentmann, and F. Reinert, Phys. Rev. Lett. 112, 226402 (2014).
[14] K. Wang, D. Graf, H. Lei, S. W. Tozer, and C. Petrovic, Phys. Rev. B 84, 220401(R) (2011).
[15] K. Wang, D. Graf, L. Wang, H. Lei, S. W. Tozer, and C. Petrovic, Phys. Rev. B 85, 041101(R) (2012).
[16] J. Park, G. Lee, F. Wolff-Fabris, Y. Y. Koh, M. J. Eom, Y. K. Kim, M. A. Farhan, Y. J. Jo, C. Kim, J. H. Shim, and J. S. Kim, Phys. Rev. Lett. 107, 126402 (2011).
[17] G. Lee, M. A. Farhan, J. S. Kim, and J. H. Shim, Phys. Rev. B 87, 245104 (2013).
[18] S. Huang, J. Kim, W. A. Shelton, E. W. Plummer, and R. Jin, PNAS 114, 6256 (2017).
[19] R. Y. Chen, S. J. Zhang, M. Y. Zhang, T. Dong, and N. L. Wang, Phys. Rev. Lett. 118, 107402 (2017).
[20] J. Y. Liu, D. Graf, T. Zou, M. Zhu, Y. Shi, S. Che, S. M. A. Radmanesh, C. N. Lau, L. Spiniu, H. B. Cao, X. Ke, and Z. Q. Mao, Nat. Commun. 8, 646 (2017).
[21] Y. Xu, Z. Song, Z. Wang, H. Weng, and X. Dai, Phys. Rev. Lett. 122, 256402 (2019).
[22] SAIMT (Bruker AXS Inc., Madison, WI, 2014).
[23] SADABS (Bruker AXS Inc., Madison, WI, 2014).
[24] G. M. Sheldrick, Acta Crystallogr. C 71, 3 (2015).
[25] International Tables for Crystallography, Volume C, edited by A. J. C. Wilson and E. Prince, 6th Edition (Kluwer Academic Publishers, Norwell, MA, 1999), p. 548.
[26] K. Schwarz, P. Blaha, and G. K. H. Madsen, Comput. Phys. Commun. 147, 71 (2002).
[27] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996).
[28] P. Larson and W. R. L. Lambrecht, J. Phys.: Condens. Matter 18, 11333 (2006).
[29] M. D. Johannes and W. E. Pickett, Phys. Rev. B 72, 195116 (2005).
[30] J. Kunes, W. KU, and W. E. Pickett, J. Phys. Soc. Jpn. 74, 1408 (2005).
[31] P. Klüfers, H. Neumann, A. Mewis, and H.-U. Schuster, Z. Naturforsch. B Chem. Sci. 35, 1317 (1980).
[32] D. Wilson, B. Sarapov, and S. Bobev, Z. Anorg. Allg. Chem. 637, 2018 (2011).
[33] N. T. Suen, Y. Wang, and S. Bobev, J. Solid State Chem. 227, 204 (2015).
[34] B. Sarapov, S. Bobev, A. Ozbay, and E. R. Nowak, J. Solid State Chem. 181, 2690 (2008).
[35] E. Brechtel, G. Cordier, and H. Schaefer, Z. Naturforsch. B 35, 1 (1980).
[36] A. F. May, M. A. McGuire, and B. C. Sales, Phys. Rev. B 90, 075109 (2014).
[37] E. Brechtel, G. Cordier, and H. Schaefer, Z. Naturforsch. B 34, 251 (1979).
[38] O. Y. Zelinska and A. J. Mar, J. Solid State Chem. 179, 3776 (2006).
[39] A. Sakopta, L. Classen, M. B. Stone, A. T. Savici, V. O. Garlea, A. Wang, J. M. Tranquada, C. Petrovic, and I. A. Zaliznyak, Phys. Rev. B 101, 041111(R) (2020).
[40] K. Wang and C. Petrovic, Phys. Rev. B 86, 155213 (2012).
[41] A. Zhang, C. Liu, C. Yi, G. Zhao, T.-L. Xia, J. Ji, Y. Shi, R. Yu, X. Wang, C. Chen, and Q. Zhang, Nat. Commun. 7, 13833 (2016).
[42] M. C. Rahn, A. J. Princep, A. Piovano, J. Kula, Y. F. Guo, Y. G. Shi, and A. T. Boothroyd, Phys. Rev. B 95, 134405 (2017).
[43] Y. F. Guo, A. J. Princep, X. Zhang, P. Manuel, D. Khalyavin, I. I. Mazin, Y. G. Shi, and A. T. Boothroyd, Phys. Rev. B 90, 075120 (2014).
[44] J. Y. Liu, J. Hu, Q. Zhang, D. Graf, H. B. Cao, S. M. A. Radmanesh, D. J. Adams, Y. L. Zhu, G. F. Cheng, X. Liu, W. A. Phelan, J. Wei, M. Jaime, F. Balakirev, D. A. Tennant, J. F. DiTusa, I. Chiorescu, L. Spinu, and Z. Q. Mao, Nat. Mater. 16, 905 (2017).

[45] S. Borisenko, D. Evtushinsky, Q. Gibson, A. Yaresko, K. Koepernik, T. Kim, M. Ali, J. van den Brink, M. Hoesch, A. Fedorov, E. Haubold, Y. Kushnirenko, I. Soldatov, R. Schäfer, and R. J. Cava, Nat. Commun. 10, 3424 (2019).

[46] K. Wang and C. Petrovic, Appl. Phys. Lett. 101, 152102 (2012).

[47] K. Zhao, E. Golias, Q. H. Zhang, M. Krivenkov, A. Jesche, L. Gu, O. Rader, I. I. Mazin, and P. Gegenwart, Phys. Rev. B 97, 115166 (2018).

[48] Y. Shiomi, H. Watanabe, H. Masuda, H. Takahashi, Y. Yanase, and S. Ishiwata, Phys. Rev. Lett. 122, 127207 (2019).

[49] H. Masuda, H. Sakai, M. Tokunaga, Y. Yamasaki, A. Miyake, J. Shiogai, S. Nakamura, S. Awaji, A. Tsukazaki, H. Nakao, Y. Murakami, T.-H. Arima, Y. Tokura, and S. Ishiwata, Sci. Adv. 2, e1501117 (2016).

[50] R. Prins and D. C. Koningsberger, editors, X-ray Absorption: Principles, Applications, Techniques of EXAFS, SEXAFS, XANES (Wiley, New York, 1988).

[51] F. Weber, A. Cosceev, S. Drobnik, A. Faiß, K. Grube, A. Nateprov, C. Pfleiderer, M. Uhlarz, and H. V. Löhneysen, Phys. Rev. B 73, 014427 (2006).

[52] Z. Haque, G. S. Thakur, R. Parthasarathy, B. Gerke, T. Block, L. Heletta, R. Pöttgen, A. G. Joshi, G. K. Selvan, S. Arumugam, L. C. Gupta, and A. K. Ganguli, Inorg. Chem. 56, 3182 (2017).

[53] O. Sologub, K. Hiebl, P. Rogl, and O. Bodak, J. Alloys Comp. 227, 40 (1995).

[54] W. Tremel and R. Hoffmann, J. Am. Chem. Soc. 109, 124 (1987).

[55] O. Prakash, A. Thamizhavel, and S. Ramakrishnan, Phys. Rev. B 93, 064427 (2016).

[56] C. Wälti, E. Felder, C. Degen, G. Wigger, R. Monnier, B. Delley, and H. R. Ott, Phys. Rev. B 64, 172515 (2001).

[57] A. Fischer, E.-W. Scheidt, W. Scherer, D. E. Benson, Y. Wu, D. Eklöf, and U. Hächsermann, Phys. Rev. B 91, 224309 (2015).

[58] Y. Y. Wang, S. Xu, L. L. Sun, and T. L. Xia, Phys. Rev. Materials 2, 021201(R) (2018).

[59] R. A. Smith, Semiconductors (Cambridge University Press, Cambridge, UK, 1978).

[60] J. Liu, P. Liu, K. Gordon, E. Emmanouilidou, J. Xing, D. Graf, B. C. Chakoumakos, Y. Wu, H. Cao, D. Dessau, Q. Liu, and N. Ni, Phys. Rev. B 100, 195123 (2019).

[61] W. Ren, A. Wang, D. Graf, Y. Liu, Z. Zhang, W. G. Yin, and C. Petrovic, Phys. Rev. B 97, 035147 (2018).

[62] C. Yi, S. Yang, M. Yang, L. Wang, Y. Matsushita, S. Miao, Y. Jiao, J. Cheng, Y. Li, K. Yamamura, Y. Shi, and J. Luo, Phys. Rev. B 96, 205103 (2017).

[63] A. A. Abrikosov, Fundamentals of the Theory of Metals (North-Holland, Amsterdam, 1988).

[64] Y. Zhang, Z. Jiang, Y.-W. Tan, H. L. Stormer, and P. Kim, Nature (London) 438, 201 (2005).

[65] D. Miller, K. Kubista, G. Rutter, M. Ruan, W. de Heer, P. First, and J. Stroscio, Science 324, 924 (2009).

[66] A. A. Abrikosov, Phys. Rev. B 58, 2788 (1998).

[67] K. K. Huynh, Y. Tanabe, and K. Tanigaki, Phys. Rev. Lett. 106, 217004 (2011).

[68] R. A. Smith, Semiconductors (Cambridge University Press, Cambridge, UK, 1978).

[69] M. M. Parish and P. B. Littlewood, Nature (London) 426, 162 (2003).

[70] Q. Bian and M. Niewczas, J. Phys. Chem. Solids 114, 45 (2018).

[71] S. N. Zhang, Q. S. Wu, Y. Liu, and O. V. Yazyev, Phys. Rev. B 99, 035142 (2019).

[72] A. E. Kovalev, S. Hill, K. Kawano, M. Tamura, T. Naito, and H. Kobayashi, Phys. Rev. Lett. 91, 216402 (2003).