Magnetic mixed valent semimetal EuZnSb2 with Dirac states in the band structure

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

We report discovery of antiferromagnetic mixed-valent semimetal EuZnSb2, 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\(^{3+}\) 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, EuZnSb2 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 momentum space host variety of quantum transport proper-

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II. EXPERIMENTAL AND THEORETICAL METHODS

Single crystals of EuZnSb2 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

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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 $\rho_{yx}$.

Powder x-ray diffraction (XRD) data were taken with Cu K$_\alpha$ ($\lambda = 0.15418$ nm) radiation of Rigaku Miniflex powder diffractometer. The element analysis was performed using an energy-dispersive x-ray spectroscopy (EDX) in a JEOL LSM-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 weighted 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 (SPECX, PHOIBOS 100) and twin anode x-ray source (SPECX, XRS50). Al K$_\alpha$ (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 K$_\alpha$ 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], which makes them clearly distinguishable and ascertains the estimated structural model, devoid of positional disorder.

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 $R_{\text{MT}}R_{\text{MT}} = 7$ and the Brillouin zone was sampled with a regular $18 \times 18 \times 3$ mesh containing 162 irreducible $k$ points to achieve energy convergence of 1 meV. A 10 000 $k$-point mesh was used for the Fermi surface calculations.

III. RESULTS AND DISCUSSIONS

The EuZnSb$_2$ refined structure [Figs. 1(a) and 1(b), Tables I and II] is ZrCuSiAs-type, Pearson index $tP8$. EuZnSb$_2$ is a ternary compound in the Eu-Zn-Sb phase diagram. The other known ternary compounds are EuZn$_2$Sb$_2$, Eu$_2$Zn$_2$Sb$_2$, Eu$_2$Zn$_4$Sb$_{18}$, and Eu$_{11}$Zn$_8$Sb$_{12}$ [31–34]. EuZnSb$_2$...
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 ZnSb₄ 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 ZnSb₄ 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) features 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$_1$–$_{1-x}$Mn$_x$–Sb$_2$ and YbMnBi$_2$ [44,45]. Topological Dirac states were also found in Zn-based 112 materials such as BaZnBi$_2$ and SrZnSb$_2$ [46,47]; EuMnBi$_2$ hosts QHE with field-tunable Eu 4 f 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]:

$$\chi(k) = \sum_{i} \frac{N_i S_i^2}{k R_i^2} f_i(k, R_i) e^{-\frac{2R_i}{\lambda}} e^{-2k^2\sigma_i^2} \sin[2kR_i + \delta_i(k)],$$

where $N_i$ is the number of neighboring atoms at a distance $R_i$ from the photoabsorbing atom, $S_i^2$ 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 $\sigma_i^2$ is the correlated Debye-Waller factor measuring the mean square relative displacement of the photoabsorber-backscatter pairs. The corrected main peak around $R \approx 2.77$ Å in Fig. 1(d) corresponds to the Zn-Sb 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-antiprismic fashion [Fig. 1(e)] with Eu-Sb1 and Eu-Sb2 bond 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 $T_N$. 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 EuZnSb$_2$ [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 $3d_{3/2}$, $3d_{3/2}$, $3d_{3/2}$, and $3d_{3/2}$, 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 $3d_{3/2}$, 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/mmm 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 might 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 3$N$, 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]:

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

where $\theta_B$ and $\theta_E$ are the Debye and Einstein temperatures, respectively, and $\alpha$ denotes the relative contribution of Debye and Einstein terms to phonon heat capacity. $\theta_B = 233$ K and $\theta_E = 73$ 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 $\Delta S = f(C_p - C_{ph+e})/dT$, and $\Delta S$ is estimated to be 11 J mol$^{-1}$ K$^{-1}$, smaller than the theoretical value $\Delta S = R\ln(2 + 1) = 17.3$ 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]:

$$\rho_{xy} = \frac{B}{e} \left(\frac{n_h\mu_h^2}{n_h + \mu_h^2} + \frac{n_e - n_h}{8} \frac{(\mu_h - n_h)(\mu_e\mu_h)^2B^2}{(\mu_h - n_e)^2}\right),$$

where $n_h$, $\mu_h$, and $\mu_e$ denote the carrier concentrations and mobilities of electrons and holes, respectively. The obtained carrier concentration and mobility are shown in FIG. 2. (a) Temperature dependence of specific heat for EuZnSb$_2$. The red line represents the fit. Inset shows the low-temperature specific heat in various magnetic field. (b) Magnetic field dependence of Hall resistivity $\rho_{xy}$ at different temperatures; two-band-model fits (see text) are shown by red lines. Inferred carrier concentration (c) and mobility (d) from the two-band fitting.
Data were measured at 2 K and the current was always perpendicular to the magnetic field direction. The Eu dependence at 2 and 30 K suggests that the magnetic order of Eu is ± predicted for up to 10% and 0 at 50 K and 9 T, which is relatively small. MR(θ) is obtained from the angular dependence of MR. As shown in Fig. 3(a), the MR angular dependence is anisotropic. It shows a crossover magnetic field B* at which the quantum limit is satisfied at specific temperature T = B* = \frac{1}{2\pi v_F}(E_F + k_B T)^2 [67] could then be used to estimate Fermi velocity. Such analysis, assuming quantum limit, gives the Fermi velocity v_F ~ 5.13 \times 10^5 \text{ ms}^{-1}, i.e., ΔLL = 5 \text{ 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 \text{ meV} for electron pocket and E_F = 250 \text{ meV} for the hole pocket, suggesting that MR arises from the first few Landau levels. Indeed, the two-band orbital magnetoresistance MR [68]

\[ MR = \frac{n_e \mu_e n_h \mu_h (\mu_e + \mu_h)^2 (\mu_0 H)^2}{(\mu_e n_h + \mu_h n_e)^2 + (\mu_0 \mu_e H^2 (\mu_0 H)^2 (n_e - n_e)^2} \]

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 EuZnSb2 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 magneto-resistance 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 EuZnSb2 is not a compensated metal with equal electron and hole concentration [Fig. 2(c)], 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(e), Table III]. The exchange interactions J_3S_3S’ = -1.810(-1.616) \text{ meV} (antiferromagnetic), J_2S_2S’ = 1.544(1.558) \text{ meV}, and J_5S = 0.856(0.663) \text{ 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 hints toward a low-field B^2 dependence to high-field linear crossover, as is sometimes observed in Dirac materials [14,15,60,61]. Semiclassical MR in metals features B^2 dependence in the low field and a saturating MR in high fields [63].

Strong external magnetic MR B^2 above which the quantum limit is satisfied at specific temperature T = B^2 = \frac{1}{2\pi v_F}(E_F + k_B T)^2 [67] could then be used to estimate Fermi velocity. Such analysis, assuming quantum limit, gives the Fermi velocity v_F ~ 5.13 \times 10^5 \text{ ms}^{-1}, i.e., ΔLL = 5 \text{ 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 \text{ meV} for electron pocket and E_F = 250 \text{ meV} for the hole pocket, suggesting that MR arises from the first few Landau levels. Indeed, the two-band orbital magnetoresistance MR [68]

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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⁺ 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 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 2c 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

### 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.

<table>
<thead>
<tr>
<th>Pattern</th>
<th>GGA</th>
<th>GGA+SO</th>
<th>GGA+U+SO</th>
</tr>
</thead>
<tbody>
<tr>
<td>AAF</td>
<td>2.88</td>
<td>4.49</td>
<td></td>
</tr>
<tr>
<td>GAF</td>
<td>1.13</td>
<td>−0.53</td>
<td></td>
</tr>
<tr>
<td>FM</td>
<td>6.46</td>
<td>7.24</td>
<td></td>
</tr>
<tr>
<td>AAF2</td>
<td>−6.23</td>
<td>−6.18</td>
<td>0</td>
</tr>
<tr>
<td>AAF3-x</td>
<td>−2.85</td>
<td>−0.04</td>
<td></td>
</tr>
</tbody>
</table>

aMagnetization along the z axis.
bMagnetization along the x axis.

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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 (2018CDJDLW0011) and Projects of President Foundation of Chongqing University (2019CDXZW002). 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.

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PHYSICAL REVIEW RESEARCH 2, 033462 (2020)


