Surface and electronic structure at atomic length scales of the non-symmorphic antiferromagnet Eu$_5$In$_2$Sb$_6$

M. Victoria Ale Crivillero,$^1$ Sahana Rößler,$^1$ Priscila F. S. Rosa,$^2$ J. Müller,$^3$ U. K. Rößler,$^4$ and S. Wirth$^1$\[email]

$^1$Max Planck Institute for Chemical Physics of Solids, Nöthnitzer Straße 40, 01187 Dresden, Germany
$^2$Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA
$^3$Institute of Physics, Goethe-University Frankfurt, 60438 Frankfurt(M), Germany
$^4$IFW Dresden, Helmholtzstrasse 20, 01069 Dresden, Germany

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We performed Scanning Tunneling Microscopy and Spectroscopy (STM/STS) measurements to investigate the Zintl phase Eu$_5$In$_2$Sb$_6$, a non-symmorphic antiferromagnet. The theoretical prediction of a non-trivial Fermi surface topology stabilized by the non-symmorphic symmetry motivated our research. On the cleaved (010) plane, we obtained striped patterns that can be correlated to the stacking of the [In$_2$Sb$_6$]$^{10-}$ double chains along the crystallographic c axis. The attempted cleavage along the a axis revealed a more complex pattern. We combined the STS measurement on non-reconstructed (010) and (081) surfaces with DFT calculations to further elucidate the electronic structure of Eu$_5$In$_2$Sb$_6$. From our investigations so far, direct experimental evidence of the predicted topological surface states remains elusive.

I. INTRODUCTION

Over the past decade, the search for materials with nontrivial electronic band topology has attracted considerable attention [1, 2]. The relevance of symmetry considerations has been put in evidence by the discovery of various novel topological phases. Non-symmorphic space groups, characterized by the inexistence of an origin that is simultaneously preserved by all symmetries, offers a suitable route to explore new topological electronic materials [3]. Indeed, there are theoretical predictions of non-trivial Fermi surface topology stabilized by the non-symmorphic symmetry [4].

Eu$_5$In$_2$Sb$_6$ crystallizes in a non-symmorphic orthorhombic structure (space group 55, Pbnm), characterized by infinite [In$_2$Sb$_6$]$^{10-}$ double chains along the crystallographic c axis [5–8]. A schematic representation of the crystal structure is presented in Fig. 1(a). The double chains, separated by three non-equivalent Eu$^{2+}$ ion sites, are constituted by two InSb$_4$ tetrahedra, bridged by Sb$_2$ dumbbell groups, see Fig. 1(b). The respective lattice parameters are $a = 12.510(3)$ Å, $b = 14.584(3)$ Å, and $c = 4.6243(9)$ Å [5]. From the chemical point of view, this structure is an example of a ternary Zintl phase, which is expected to have a precise electron transference and therefore to show insulating behavior. Interestingly, the isostructural compound Ba$_3$In$_2$Sb$_6$ (paperwork group pgg) was predicted to host topological surface states on the (001) surface [9]. Very recent band structure calculations suggested a similarly non-trivial topology for the (001) surface of the magnetic analog Eu$_5$In$_2$Sb$_6$ [10], a claim which calls for experimental verification.

The inclusion of Eu$^{2+}$ ions into the Zintl phase gives rise to magnetism [8, 11]. The particular arrangement of the 4f localized moments dictates a complex, presently not fully elucidated, magnetic structure. At low temperatures, two antiferromagnetic transitions ($T_{N1} \approx 14$ K and $T_{N2} \approx 7$ K) have been reported [8]. Notably, Eu$_5$In$_2$Sb$_6$ exhibits a negative magnetoresistance (MR) that increases strongly upon decreasing the temperature below about 15$T_{N1}$ and reaches a colossal MR (CMR) value of $-99.999\%$ at 9 T and 15 K, just above $T_{N1}$ [8]. Concomitant with the rapid increase of the MR, an anomalous Hall effect (AHE) is observed as well as a deviation of the susceptibility from a Curie-Weiss-type behavior.

The occurrence of CMR in low-carrier density materials containing Eu$^{2+}$ has been linked to the emergence of quasiparticles called magnetic polarons [12, 13]. Indeed, the existence of local inhomogeneities in the electronic density of states at the surface of EuB$_6$ has recently been seen by scanning tunneling microscopy and spectroscopy (STM/STS) and was interpreted as the localization of charge carriers due to polaron formation [14]. It is, however, important to note that most of these CMR materials, ranging from EuB$_6$ [15] to manganites [16], exhibit ferromagnetic order. In contrast, Eu$_5$In$_2$Sb$_6$, together with EuTe [17] [18] and Eu$_{14}$MnBi$_{11}$ [19], are candidates for realizing polarons in an antiferromagnet. We note here that magnetic polarons in antiferromagnets are explored only scarcely, see e.g. [20] for a review.

Here, we report on STM/STS measurements in order to obtained local insights into the electronic structure and surface morphology of the Zintl phase Eu$_5$In$_2$Sb$_6$, a non-symmorphic antiferromagnet. We combine the STS measurements with DFT calculations to further elucidate the density of states (DOS). This work presents, to the best of our knowledge, the fist report of the surface structure of an Eu-based ternary Zintl phase.

* Steffen.Wirth@cpfs.mpg.de
II. EXPERIMENTAL DETAILS

The single crystals investigated in this work were grown using a combined In-Sb self-flux technique [8]. The rod-like shaped crystals have typical sizes of 0.5 mm × 0.2 mm × 3 mm, with the c axis being the long sample axis, see Fig. 1(d). The crystallographic structure was verified by X-ray diffraction using a MWL120 real-time back-reflection Laue camera system. Specific heat measurements were performed using a commercial calorimeter that utilizes a quasi-adiabatic thermal relaxation technique.

STM/STS was conducted in a commercial low temperature STM (base temperature ≈ 4.6 K) under ultra-high vacuum (UHV) condition, p ≤ 3 × 10⁻⁹ Pa [21], using electrochemically etched tungsten tips. For tunneling spectroscopy, a small ac voltage \( V_{mod} \) was added to the bias voltage \( V_b \) and a standard lock-in detection technique was applied. Some of the reported STM data were obtained with a dual-bias mode: two different bias voltages were applied for the forward and backward scans. Therefore, the two topographies were obtained quasi-simultaneously under otherwise effectively identical conditions, and specifically within identical areas. If not stated otherwise, the presented STM/STS results were acquired at base temperature. In addition, we also conducted STM/STS measurements at elevated temperatures, 5.9 K ≤ T ≤ 17 K, using a resistively heated sample holder. This allowed us to study the temperature evolution of the local density of states (LDOS) across both \( T_{N1} \) and \( T_{N2} \) at atomically resolved length scales.

We attempted to cleave a total of 8 single-crystals in situ and at low temperatures (\( T \approx 20 \) K) along the main macroscopic sample axes. As inferred from the diffraction results, those directions are expected to conform with the crystallographic a, b and c axes. However, as a result of the subtle anisotropy in the \( ab \) plane, in some cases further analysis will be needed to unambiguously verify the crystallographic in-plane sample orientation. In Table 1, details of five surfaces are presented which were studied in depth. On the remaining samples, atomically flat surface areas were not found.

The electronic structure of Eu₃In₂Sb₆ was also examined by calculations using density functional theory (DFT). The calculations were performed using the full-potential local orbital (FPLO) approach [22] as implemented in the fplo code [23]. We used the generalized gradient approximation (GGA) as exchange-correlation functional [24]. The magnetic 4f configuration of Eu²⁺ is expected to remain in the \( L = 0 \) and \( S = 7/2 \) groundstate in Eu₃In₂Sb₆. Therefore, we applied the open core approach, which places a correspondingly occupied 4f shell on the Eu site—in this case an isotropic shell with a net spin of 7/2. This entirely removes the 4f levels from the valence band structure [25, 26], while keeping 4f-5d exchange interactions on site and, thus, allows for indirect exchange couplings via the valence electrons between the Eu-spin moments. Such a fully localized limit for the 4f electronic states on Eu²⁺ enabled us to impose various magnetic configurations on the complex crystal structure of Eu₃In₂Sb₆ and to estimate their energies in a simplified fashion. Within this method, we explored various collinear spin structures in an effort to

| Sample | #1 | #2 | #3 | #4 | #5 |
|---------|----|----|----|----|----|
| Attempted plane | ac | bc | ac | ab | ab |
| Assigned plane | (081) | ? | ac | ab | ab |
| surface quality | many | / extended | atomically | defects | terraces | rough |

FIG. 1. Crystal structure of Eu₃In₂Sb₆: (a) Perspective projections as viewed along the [001] axis and (b) cut along the \( ab \) plane depicting the three groups of crystallographically unique Eu atoms, Eu(1), Eu(2), and Eu(3), labeled respectively as 1, 2, and 3 for simplicity. (c) Specific heat, \( C_p \), as a function of temperature in zero applied magnetic field. (d) X-ray Laue patterns along the crystallographic \( b \) axis. (e) Photograph of an exemplary Eu₃In₂Sb₆ single crystal. (f) Resistivity \( \rho(T) \) as measured in \( ab \)-plane; inset: estimates of the activation energy (see text).
examine possible magnetic ground states of Eu$_5$In$_2$Sb$_6$. These calculations of different magnetic configurations were conducted within the scalar relativistic approach. In addition, band structures were also evaluated by fully relativistic calculations. Here, the fully relativistic FPLO code includes spin orbit coupling (SOC) to all orders, being based on solutions of the 4-spinor Kohn-Sham-Dirac equations.

The calculations of the electronic band-structure of Eu$_5$In$_2$Sb$_6$ were based on the experimental lattice structure as determined in Ref. 5. For comparison, we also calculated the electronic band-structure for the non-magnetic analogue Ba$_5$In$_2$Sb$_6$, for which experimental structure data were taken from Ref. 28.

### III. RESULTS

#### A. Characterization of Eu$_5$In$_2$Sb$_6$ single crystals

Figure 1(c) shows the temperature dependence of the specific heat, $C_p$, in zero magnetic field of a representative Eu$_5$In$_2$Sb$_6$ single crystal. The overall behavior and more specifically the two antiferromagnetic transitions at $T_{N1} = 14.1$ K and $T_{N1} = 7.3$ K are in good agreement with those previously reported [8]. The $H$–$T$ phase diagrams of Eu$_5$In$_2$Sb$_6$ along the three main crystallographic axes, constructed using a combination of magnetization and heat capacity measurements, will be reported elsewhere.

Figure 1(e) presents a representative x-ray Laue pattern along the crystallographic $b$ axis. For all the single-crystals inspected by x-ray the main macroscopic sample axes conform with the crystallographic $a$, $b$, and $c$ axes, with the shortest sample side parallel to the $b$ axis.

Eu$_5$In$_2$Sb$_6$ has been classified as a narrow-gap semiconductor [5, 6, 8]. This can be inferred from the bulk resistivity $\rho(T)$, see Fig. 1(f). From fits to $\rho(T) \propto T^n \exp(-E_a/k_B T)$, activation energies $E_a$ between 45–50 meV were estimated (for 36 K $\lesssim T \lesssim 120$ K) depending on whether an Arrhenius ($n = 0$) or small polaron hopping conduction mechanism ($n = 1$) [29] was assumed [inset to Fig. 1(f)]. These values of $E_a$ are in excellent agreement with those of Ref. 8 while much larger values were reported in Ref. [6].

#### B. STM: Topography

Interestingly, we found stable tunneling conditions only using relatively large bias voltages $V_b$. In Fig. 2(d) and (e) the STM topography of an atomically flat area of $10 \times 10$ nm$^2$ on sample #1, obtained in dual-bias mode at $T = 5.9$ K and $I_{sp} = 1.4$ nA. (a) $V_b = +2$ V; (b) $V_b = -2$ V. (c) and (d): Height profiles along the marked lines in (a) and (b), respectively. (e) Schematic representation of a proposed surface termination cleaved along the plane (081). Here, the horizontal separation $\Delta x = 2.0$ nm between the stripes is marked. (f) Perspective view: the exposed tetrahedra constituting the stripes along the $a$-axis are separated by 1.25 nm, in agreement with the measurement in (c).
overview of different atomically flat surfaces encountered on samples #1 and #2 is presented ($V_b = \pm 2\,\text{V}$). These samples were attempted to be cleaved along the nominal $a$ axis, i.e. the $bc$ plane is expected to be exposed. In general, this kind of topography has to be searched for; as mentioned above, on some cleaved sample surfaces we did not succeed to find atomically flat areas at all. One principal axis can easily be identified in most cases, the orientation of which corresponds to the crystallographic $c$ axis. The types of observed topographies ranges from more disordered ones, Fig. 2(a), to almost defect-free surfaces with step edges, Fig. 2(d). Clearly, the diversity of observed topographies puts in evidence that Eu$_5$In$_2$Sb$_6$ surfaces are prone to manifest complex configurations, which reinforces the relevance of studying the surface properties with a local probe as STM/STS.

The two representative topographies in Figs. 2(c) and (d) exhibit atomically flat areas separated by sub-nanometer-high step edges. They were observed on two different samples, #1 and #2, over areas of $10 \times 10\,\text{nm}^2$ and $20 \times 20\,\text{nm}^2$, respectively. The average height of the step edges is $0.50\,\text{nm}$, as seen from the line scan in Fig. 2(e) taken along the turquoise line in Fig. 2(c). The distance between corrugations along the $c$-axis in the upper plane is about $0.84\,\text{nm}$. Noticeably, there is a displacement between the corrugations within the two adjacent planes; compare, for example, the orange and green line scans in Fig. 2(f). In this case, the distances between corrugations ($\Delta x \approx 1.87\,\text{nm}$, $\Delta y \approx 0.84\,\text{nm}$) and the step height $\Delta z \approx 0.50\,\text{nm}$ did not match with the expected values for a non-reconstructed $bc$ plane.

On sample #1, a different type of atomically flat pattern could be observed, see Fig. 3. Again, the topographies in Figs. 3(a) and (b) were obtained in dual-bias mode, i.e. with $V_b = +2\,\text{V}$ and $-2\,\text{V}$, respectively. In this case, the double-stripe-like corrugations are separated by $\Delta y \approx 1.94\,\text{nm}$, while the distance of corrugations along the stripe direction is $\Delta x \approx 1.24\,\text{nm}$. The closeness of latter distance to the lattice parameter $a$ suggests that the cleaved surface may contain the crystallographic $a$ axis. To further identify the surface plane, we searched in the crystal structure for planes separated by $1.94\,\text{nm}$. A suitable candidate is the (081) plane; see the schematic representations in Figs. 3(c) and (f). In that case, the distance between the exposed tetrahedra along the $a$-axis is $a$, while the horizontal separation between the so-formed stripes is $2.00\,\text{nm}$. The tilting angle between the (081) plane and the $ac$ plane is $22^\circ$. Noticeably, some crystals exhibit facets at $\sim 30^\circ$ from the $a$-axis. Therefore, a plausible scenario is that this sample was mounted parallel to one of those facets before cleaving such that the crystal was then cleaved along the (081) plane. Regarding the topographies Fig. 3(a) and (b), it is worth noting three observations. First, there is a noticeable difference in contrast for the two $V_b$-values applied (see also Fig. 4) suggesting a complex energy and spatial dependence of the types of states dominating the tunnel current. Second, this type of pattern extends over relatively large areas without step edges. Third, there is an appreciable number of defects observed.

To gain further insight into the dependence of the contrast in topography on $V_b$, a series of 5 images of the same area was taken in dual-bias mode (positive and negative $V_b$) with $|V_b|$ increasing from 1–4 V, see Fig. 4. Note that these images were obtained on the same cleave and close to the area shown in Figs. 3(a), (b). While the contrast is strongly enhanced for positive $V_b$, there is no
FIG. 5. Topography of non-reconstructed, atomically flat surfaces cleaved along the ac plane (sample #3). (a) and (b): STM topographies obtained with $V_b = -3$ V and $I_{sp} = 1.4$ nA at $T = 7.0$ K and $T = 5.9$ K, respectively. (c) and (d): Height profiles along the corresponding lines marked in (a) and (b). (e) Schematic representation of the proposed Sb-terminated surface cleaved along the ac plane and a corresponding sub-unit cell terrace. Note that for simplicity only the tetrahedra are shown. Their double-chain stacking imposes a lateral spacing of the protrusions of $a = 1.25$ nm along the $a$-axis and a vertical distance to the next Sb-terminated surface $\frac{1}{2} b = 0.73$ nm. (f) Alternative Eu-terminated (010) plane formed by breaking the Sb dumbbell bonds during the cleaving. The resulting height-modulated surface also exhibits a 1.25 nm period along $a$ and 0.73 nm step edges along $b$.

FIG. 6. (a) Averaged spectra taken at 5.9 K on two atomically flat surfaces of Eu$_5$In$_2$Sb$_6$: the non-reconstructed ac plane, S1, and the (081) plane, S2. The insets present the corresponding topographies. (b) $T$-dependence of $dI/dV$-spectra on S2 covering temperatures below, in between and above $T_{N1}$ and $T_{N2}$.

Motivated by the results presented above, the following contrast reversal or lateral shift of corrugations observed upon reversing $V_b$, neither for the regular features nor for the defects. These observations are consistent with an above-indicated assignment of the regularly arranged protrusions to negatively charged Sb in either the InSb$_4$ tetrahedra or the Sb$_2$ dumbbells, cf. Figs. 5(e), (f). However, to fully interpret the STM topographies, a comparison with simulated STM images will be required.

Sample #3 was attempted to be cleaved along the ac plane. Here, we were able to locate some areas where the in-plane arrangement of corrugations and the height of step edges match the values expected for an ac surface. In Fig. 5 we present a striped pattern with a lateral spacing of 1.2 nm, while the height difference between terraces is $0.75 \, \text{nm} \approx \frac{1}{2} b$. Notably, the density of defects, apart from the step edges, is very low. This arrangement can be nicely correlated to the double-chain stacking, where each stripe corresponds to the end-part of the chains, see Fig. 5(e), constituting a Sb-terminated surface. An alternative scenario arises by considering the surface composed by the Eu(1) and Eu(2) ions and formed by breaking the Sb dumbbell bonds during the cleaving process, cf. Fig. 5(f), again forming a height-modulated surface with periodicity $a$ and possible step edges of $\frac{1}{2} b$. On both types of terminations, there is an in-plane displacement between the corrugations on both sides of a step edge, cf. Figs. 5(e) and (f); the expected value
TABLE II. Results of total energies calculated by DFT for different spin configurations in Eu₃In₂Sb₆ and the spin-moments on the Eu sites of the three different sublattices. The spin configurations FM, FiM, and AFM represent ferromagnetic, ferrimagnetic, and antiferromagnetic ones, respectively, as illustrated in Fig. [except FM].

| Name | Magnetic spin moments | Energy relative to AFM-a |
|------|-----------------------|--------------------------|
|      | (Eu(1))(Eu(2))(Eu(3)) | | meV/unit cell |
| FM   | ↑↑↑↑↑↑   | 2.144 | 0 |
| FiM  | ↑↑↑↑↑↑   | 2.144 | 0 |
| AFM-a| ↑↑↑↑↑↑   | 2.144 | 0 |
| AFM-c| ↑↑↑↑↑↑   | 2.144 | 0 |
| AFM-b| ↑↑↑↑↑↑   | 2.144 | 0 |

in the Sb-terminated scenario is 0.21 nm and for the Eu-terminated one 0.19 nm. Unfortunately, the small difference between the values and the lack of atomic resolution along the c axis renders an identification of the surface termination challenging. Nonetheless, the small difference of the Eu(1) positions along b direction and the expected asymmetry of the stripes along a make an Eu-terminated surface less likely. Also from an energetic point of view, an Eu-terminated surface appears unfavorable considering the involved Sb₂-Sb₂ bond-breaking. Yet, further surface energy calculations are needed to assess the surface termination.

Finally, motivated by the predictions of topological surface states on the (001) surface of Ba₃In₂Sb₆ [9], we attempted to cleave samples #4 and #5 along the c axis. Unfortunately, and despite exhaustive efforts, atomically flat surface areas could not be found. Intuitively, the experimental absence of ordered flat surfaces may be understood by considering that the breaking of the double chains is very likely unfavorable.

C. STS

An overview of the local conductance, \( g(V,T) = \frac{dI(V)}{dV} \), as measured by STS, is presented in Fig. 6. A comparison of the results obtained on two atomically flat surfaces at 5.9 K is presented in Fig. 6(a): the non-reconstructed ac surface of sample #3, here called S1, and the (081) plane of sample #1, denoted S2. Albeit \( g(V) \) of both spectra span several orders of magnitude (note the logarithmic scale) within the range \(-2 V \leq V_b \leq +2 V \) with deep, yet finite minima, there are clear differences: i) \( g(V) \) is significantly higher on S2, specifically for \( V_b \leq 0 \). ii) While the minimum of \( g(V) \) is very close to \( V_b = 0 \) for S1, it appears to be shifted to \( V_b \approx 260 \text{ mV} \). iii) The gap width appears to be slightly smaller on S2. Likely, these observations result from the more disturbed surface with larger defect density of S2, given the insulating behavior of Eu₃In₂Sb₆ at this low temperature. However, it should be emphasized that the measured \( g(V) \)-values remain finite within the pseudo gap even for the well-ordered surface S1.

The temperature dependence of \( g(V,T) \) was studied on surface S2, see Fig. 6(b). In particular, we repeated the measurements below and above \( T_{N1} \) and \( T_{N2} \) several times in order to evaluate any possible influence of the antiferromagnetic order on \( g(V,T) \). At all temperatures, the minimum of \( g(V,T) \) is found at positive \( V_b \). In general, there is no significant difference between the spectra taken at 10 K and 17 K, i.e. around \( T_{N1} = 14.1 \text{ K} \). In contrast, below \( T_{N2} = 7.3 \text{ K} \) [see spectrum at \( T = 5.9 \text{ K} \) in Fig. 6(b)] the conductance at \( V_b = 0 \), and therefore the LDOS at the Fermi level, is increased by almost one order of magnitude.

D. Density Functional Theory calculation

In order to calculate the DOS of the ground state using DFT, it is necessary to first determine the ground state magnetic configuration. In consequence, we start by describing the calculation of energies for the different magnetic configurations, and subsequently, calculate the DOS of the energetically most favourable configurations.

1. Magnetic configurations

Eu₃In₂Sb₆ contains ten Eu ions in the ab base plane of the unit cell. These sites belong to three different Wyckoff positions of the space group \( \text{Pbam} \): Eu(1) and Eu(3) both occupy two different sets of 4g sites and Eu(2) the 2a sites. In order to probe possible magnetic configurations, we have conducted DFT calculations for all combined magnetic states that can be created from either fully saturated ferromagnetic (FM) or fully compensated antiferromagnetic (AFM) collinear spin-configurations of these three magnetic sub-systems, amounting to 128 magnetic configurations. The calculations were executed with the scalar relativistic DFT approach and using the open-core method. The four configurations with lowest calculated energies are sketched in Fig. 7. The corresponding energies with respect to the AFM-a state and the magnetic spin-moments are listed in Table II. The A-type configuration has ferromagnetically coupled Eu spin moments in the ab-plane, that are alternatingly stacked in an antiparallel staggered order. Such a spin configuration is very close to the ground state. In particular, the small difference between the values and the lack of atomic resolution along the c axis renders an identification of the surface termination challenging. Nonetheless, the small difference of the Eu(1) positions along b direction and the expected asymmetry of the stripes along a make an Eu-terminated surface less likely. Also from an energetic point of view, an Eu-terminated surface appears unfavorable considering the involved Sb₂-Sb₂ bond-breaking. Yet, further surface energy calculations are needed to assess the surface termination.
FIG. 7. Magnetic configurations of lowest energy according to DFT calculations: (a)–(c) fully compensated antiferromagnetic (AFM) states from collinear DFT (spin resolved). (d) first ferrimagnetic (FiM) configuration. The crystallographic orientation conforms to the one in Fig. 1(b).

In addition, for the antiferromagnetic configurations with lowest energies, fully relativistic calculations were conducted. The corresponding results suggest that: i) The effective coupling between the Eu-layers likely is ferromagnetic. ii) There are strong antiferromagnetic couplings within the ab-plane between Eu-ions within the three sublattices of Eu(1)-, Eu(2)- and Eu(3)-sites. iii) The close match of energies for the different AFM and the ferrimagnetic configuration indicates that this multi-sublattice spin system is likely frustrated. The reason is presumably geometric frustration related to triangular and pentagonal elementary plaquettes between nearest-neighbor Eu-sites. In consequence, the correct magnetic ground state of Eu$_5$In$_2$Sb$_6$ is likely a complex non-collinear AFM or ferrimagnetic state to lift this frustration. However, magnetic couplings beyond next neighbors may also play a role. The magnetic exchange mechanism between the Eu$^{2+}$-ions is likely of the Ruderman-Kittel-Kasuya-Yosida (RKKY)-type which can support long-range contributions, both in-plane and out-of-plane. Our restricted computational results do not allow a complete computational determination of the magnetic ground state which includes these intricacies.

It is noteworthy that the lowest energy magnetic configurations do not break inversion symmetry and, if no cell doubling is enforced by these long-range couplings, the system of magnetic Γ-point modes calculated is complete in the so-called exchange approximation. If the magnetic ground-state of Eu$_5$In$_2$Sb$_6$ is described by a suitable combination of such Γ-point modes, a relatively simple spin structure with compensated moments may approximately describe this magnetic system. However, in that case spin-orbit coupling (SOC) does allow for the occurrence of weak ferromagnetism by spin-canting in this orthorhombic magnetic crystal [32], as the Dzyaloshinskii-Moriya exchange is allowed. In fact, experimental data on Eu$_5$In$_2$Sb$_6$ revealed a very small in-plane ferromagnetic component and hysteresis which was ascribed to the complex magnetic structure with canted moments [8]. As such, the intrinsic weak ferromagnetism may be linked to the primary AFM Γ-point order.

Sizeable effects by SOC are seen in the results of fully relativistic (fr) calculations with different quantization axes in Table I. From an experimental point of view, this feature was found to be an important aspect.
a determination of the magnetic ground state and a detailed understanding of the magnetic field–temperature phase diagram for Eu$_5$In$_2$Sb$_6$ will require major efforts. Our theoretical results, however, suggest that the basic spin structure is antiferromagnetic within the $ab$ plane. A simple A-type antiferromagnetic structure appears unlikely. Nonetheless, the evaluation of the electronic band structure below is based on the collinear low-energy spin structures (Fig. 7) which are expected to approximate the essential features of ordered magnetism in Eu$_5$In$_2$Sb$_6$.

2. Electronic band structure

In an effort to gain further insight into the band structure of Eu$_5$In$_2$Sb$_6$ and to allow for comparison to our STS results (Fig. 6), the electronic density of states (DOS) for both the ferromagnetic (FM) and the AFM spin configuration AFM-a with lowest energy were calculated, see Fig. 8. In addition, the DOS of the non-magnetic isostructural compound Ba$_5$In$_2$Sb$_6$ is shown. All three systems behave as semi-metals with a small DOS near the Fermi energy $E_F$. Qualitatively, the gap-like features observed for Eu$_5$In$_2$Sb$_6$ in both the calculations and the STS data even share the asymmetry of a somewhat steeper rise for positive energies compared to the negative side.

A closer inspection of the energy region near $E_F$ (Fig. 9) reveals a significant difference between the FM and the AFM configuration. The AFM state with compensated total moments has a significant depression of the DOS.

FIG. 9. DOS near the Fermi energy $E_F$ (at zero energy). A comparison between fully relativistic (fr) and scalar relativistic (sr) DFT calculations for Eu$_5$In$_2$Sb$_6$ in FM and AFM spin configuration as well as Ba$_5$In$_2$Sb$_6$ is shown.

right at $E_F$ compared to the FM state. These results for the AFM state are also in line with the STS data discussed above. The comparison of fully-relativistic (fr) and scalar relativistic band structure calculations near $E_F$ also shows a remarkable re-distribution and more structured DOS for the former, but it does not change the overall picture.

In an effort to gain insight into a possible nontrivial electronic band topology of Eu$_5$In$_2$Sb$_6$, the momentum-resolved band structure as obtained by a scalar relativistic DFT calculation for AFM-a configuration is presented in Fig. 10. Clearly, there are certain spin-split bands crossing $E_F$ in the AFM state, see section along X–S–Y in the energy-enlarged inset. These results are in good agreement with those obtained by other band structure calculations [10]. It should be noted, however, that care has to be taken when comparing results of different calculation schemes: On the one hand, the magnetism of Eu$_5$In$_2$Sb$_6$ is included in our calculations. On the other hand, SOC is only considered in the fully relativistic calculations presented in Fig. 9 while it is neglected in the scalar relativistic ones. Our calculations do not provide any indication for a non-trivial band topology, in line with a trivial $Z_2$ index proposed in Ref. [33]. This is consistent with our STS data, at least for the surfaces investigated so far. Nonetheless, to scrutinize the surface topology in Eu$_5$In$_2$Sb$_6$, the topological invariants for the double-glide (001) surface should be explored by Wilson loop calculations, similar to those for Ba$_5$In$_2$Sb$_6$ in Ref. [10].

IV. DISCUSSION AND CONCLUSIONS

Eu$_5$In$_2$Sb$_6$ was successfully cleaved in situ and patches of atomically flat areas, specifically for the $ac$ surface
plane, were located. Within such areas, our STS data indicated gap-like spectra with a very low, but finite conductance at the Fermi level. Qualitatively, the STS data agree with the calculated DOS in the energy range from $-1$ to $+1$ eV. The calculated band structures and resultant DOS for the AFM and FM spin structures in Eu$_5$In$_2$Sb$_6$ ultimately illustrate how the difference in spin configuration can lead to a re-organization of the small band contributions near $E_F$. Apart from such subtlety, the major influence of the underlying Eu $4f$ spin structure suggests a rather traditional picture for the electronic properties of this compound. In the AFM state, the material has only rather few charge carriers available, and the AFM background allows only for incoherent hopping transport via thermal activation, which may lead to an effective insulator-like behavior as indeed observed experimentally. In particular, a negative temperature coefficient of the resistivity, $d\rho/dT < 0$ may be caused by the stiffening of the AFM correlations upon lowering the temperature and even through the magnetic phase transitions. For decreasing temperature and/or under applied magnetic field, spin-polarons can be formed and may lead to strongly improved conduction, resulting in a CMR behavior. The enhanced DOS in the FM state shows [see Fig. 8(b)], how such a spin-polarized electronic structure generates charge carriers.

At present, neither our band structure calculations for the AFM-a state nor the STS results at low temperature provide any indication for a non-trivial band topology of Eu$_5$In$_2$Sb$_6$. Nonetheless, our future experimental efforts will focus on an optimization of cleaved (001) surfaces as atomically flat surfaces of this orientation appear to be essential for conclusive results concerning the topological nature of Eu$_5$In$_2$Sb$_6$.

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[1] T. Zhang, Y. Jiang, Z. Song, H. Huang, Y. He, Z. Fang, H. Weng, and C. Fang, Nature 566, 475 (2019).
[2] F. Tang, H. C. Po, A. Vishwanath, and X. Wan, Nature 566, 486 (2019).
[3] Z. Wang, A. Alexandradinata, R. J. Cava, and B. A. Bernevig, Nature 532, 189 (2016).
[4] S. A. Parameswaran, A. M. Turner, D. P. Arovas, and A. Vishwanath, Nat. Phys. 9, 299 (2013).
[5] S.-M. Park, E. S. Choi, W. Kang, and S.-J. Kim, J. Mater. Chem. 12, 1839 (2002).
[6] S. Chanakian, U. Aydemir, A. Zevakhink, Z. M. Gibbs, J.-P. Fleurial, S. Bux, and G. J. Snyder, J. Mater. Chem. C 3, 10518 (2015).
[7] M. Radziewski, F. Stegemann, S. Kleiner, Y. Zhang, B. P. T. Fokwa, and O. Janka, Mater. Chem. Front. 4, 1231 (2020).
[8] P. F. S. Rosa, Y. Xu, M. Rahn, J. Souza, S. Kushwaha, L. Veiga, A. Bombardi, S. Thomas, M. Janoschek, E. Bauer, et al., npj Quantum Mater. 5, 52 (2020).
[9] B. J. Wieder, B. Bradlyn, Z. Wang, J. Cano, Y. Kim, H.-S. D. Kim, A. M. Rappe, C. L. Kane, and B. A. Bernevig, Science 361, 246 (2018).
[10] Yuanfeng Xu (2022), private communication.
[11] U. Subbarao, S. Sarkar, B. Joseph, and S. C. Peter, J. Alloys Comp. 658, 395 (2016).
[12] T. Kasuya and A. Yanase, Rev. Mod. Phys. 40, 684 (1968).
[13] S. von Molnar, Sensors and Actuators A: Physical 91, 161 (2001).
[14] M. Pohl, S. Rößler, Y. Ohno, H. Ohno, S. von Molnár, Z. Fisk, J. Müller, and S. Wirth, Phys. Rev. Lett. 120, 257201 (2018).
[15] S. Süßow, I. Prasad, S. Bogdanovich, M. C. Aronson, J. L. Sarrao, and Z. Fisk, J. Appl. Phys. 87, 5591 (2000).
[16] M. B. Salamon and M. Jaime, Rev. Mod. Phys. 73, 583 (2001).
[17] N. J. Oliveira, Jr., S. Foner, Y. Shapira, and T. B. Reed, Phys. Rev. B 5, 2634 (1972).
[18] Y. Shapira, S. Foner, N. F. Oliveira, Jr., and T. B. Reed, Phys. Rev. B 5, 2647 (1972).
[19] J. Y. Chan, S. M. Kauzlarich, P. Klavins, R. N. Shelton, and D. J. Webb, Phys. Rev. B 57, R8103 (1998).
[20] S. von Molnár and P. A. Stampe, in Handbook of Magnetism and Advanced Magnetic Materials, edited by H. Kronmuller and S. Parkin (John Wiley & Sons, Ltd., 2007), vol. 5, pp. 2689–2702.
[21] Scienta Omicron GmbH, Taunusstein (Germany).
[22] K. Koepernik and H. Eschrig, Phys. Rev. B 59, 1743 (1999).
[23] Calculations have been performed using fplo18.00, URL https://www.fplo.de
[24] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996).
[25] M. S. S. Brooks, L. Nordström, and B. Johansson, J. Phys.: Condens. Matter 3, 3393 (1991).
[26] M. S. S. Brooks, L. Nordström, and B. Johansson, J. Phys.: Condens. Matter 3, 2357 (1991).
[27] M. Richter, J. Phys: D: Appl. Phys. 31, 1017 (1998).
[28] G. Cordier and M. Stelter, Z. Naturforsch. 43b, 463 (1988).
[29] D. Emin and T. Holstein, Ann. Phys. 53, 439 (1969).
[30] H. Möning, M. Todorović, M. Z. Baykara, T. C. Schwoember, L. Rodrigo, E. I. Altman, R. Pérez, and U. D. Schwarz, ACS Nano 7, 10233 (2013).
[31] T. Woolcot, G. Teobaldi, C. L. Pang, N. S. Beglitis, A. J. Fisher, W. A. Hofer, and G. Thornton, Phys. Rev. Lett. 109, 156105 (2012).

[32] A. N. Bogdanov, U. K. Rößler, M. Wolf, and K. H. Müller, Phys. Rev. B 66, 214410 (2002).

[33] N. Varnava, T. Berry, T. M. McQueen, and D. Vanderbilt, Engineering magnetic topological insulators in $\text{Eu}_5M_2X_6$ Zintl (2022), arXiv:2203.06212.