Spin and orbital transport in rare earth dichalcogenides: The case of EuS_2

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We perform first-principles calculations to determine the electronic, magnetic and transport properties of rare-earth dichalcogenides taking a monolayer of the H-phase EuS_2 as a representative. We predict that the H-phase of the EuS_2 monolayer exhibits a half-metallic behavior upon doping with a very high magnetic moment. We find that the electronic structure of EuS_2 is very sensitive to the value of Coulomb repulsion U, which effectively controls the degree of hybridization between Eu-f and S-p states. We further predict that the non-trivial electronic structure of EuS_2 directly results in a pronounced anomalous Hall effect with non-trivial band topology. Moreover, while we find that the spin Hall effect closely follows the anomalous Hall effect in the system, the orbital complexity of the system results in a very large orbital Hall effect, whose properties depend very sensitively on the strength of correlations. Our findings thus promote rare-earth based dichalcogenides as a promising platform for topological spintronics and orbitronics.

I. INTRODUCTION

Two-dimensional (2D) transition-metal dichalcogenides (TMDs) have attracted enormous attention due to their strong potential as a platform for various flavors of spintronics effects. The rich set of electronic phases that TMDs exhibit includes semiconductors [1–3], semimetals [4], metals [5], and superconductors [6], which allows for novel design paradigms incorporating multiple complex phases of matter. Furthermore, due to a combination of low crystal symmetry and spin-orbit coupling (SOC) [7], these materials can host exotic excitations and exhibit different transport properties. For example, recent studies suggest that TMDs naturally lacking inversion symmetry can be exploited to drive a variety of Hall effects such as the anomalous Hall effect (AHE) [8], valley Hall effect [9, 10], spin Hall effect (SHE) [11, 12], or even orbital Hall effect (OHE) [13–23].

Among the latter two phenomena, SHE and OHE attract particular attention owing to bright prospects for spintronic applications [24–27]. While the SHE is a well-known and by now in-depth studied phenomenon [28], the OHE is much less explored [18, 20–22, 25]. The essence of the OHE is in the coupling between the orbital motion of electrons and an electric field, which drives a transverse flow of orbital angular momentum, as opposed to spin angular momentum in SHE [13, 15, 18, 29–31]. Such orbital Hall currents can for example generate a measurable effect via the generation of orbital type of torques on the magnetization [32, 33], or give rise to strong non-local spin currents via the effect of spin-orbit coupling [34]. This also gives rise to a new channel for information transfer − the orbital channel. Harnessing the physics of orbital currents is expected to push spintronics into a new direction, the direction of orbitronics [35].

On the side of materials, OHE has been studied predominantly in non-magnetic crystals, and very little is known about orbital currents in magnetic systems, especially in low dimensions. In this light, magnetism in 2D materials can be extremely profitable for spintronics and orbitronics [36–38]. Recent discoveries of magnetic order in various classes of 2D magnets such as CrI_3 [39], Fe_3GeTe_2 [40], and bilayer $Cr_2Ge_2Te_6$ [41, 42] have given the exploration of novel 2D ferromagnetic materials and their magnetic properties a significant momentum. On the side of TMDs, several representative compounds, such as metallic VX_2 [43–45], CrX_2 [45–47] and semiconducting MnS_2 (X=S, Se, Te) [45, 48, 49], have been shown to exhibit magnetic ordering in their ground state. A very promising direction to pursue here is the realization of 2D magnetic materials, and in particular dichalcogenides, based on $4f$-elements. Given a strong tendency to magnetism and strong SOC combined with orbital complexity of $4f$-electrons, $4f$-based 2D materials are expected to serve as a fruitful foundation for various spin and especially orbital transport effects.

In this work, we perform first-principles calculations of structural, electronic, magnetic and transport properties of H-phase monolayer of the $4f$ rare-earth dichalcogenide EuS_2. Taking EuS_2 as an example, we thus aim to uncover the potential of the $4f$ rare-earth dichalcogenides as possible sources of pronounced charge, spin, and orbital currents. Keeping in mind the importance of correlation effects in f-materials, we consider a range of Coulomb strengths as given by the parameter U, finding that EuS_2 has a very large magnetic moment and a large band gap for a wide range of correlation strengths. Importantly, we

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find a strongly increased $p-d-f$ hybridization among Eu and S atoms upon increasing U, which has a drastic influence on the transport properties. Specifically, our calculations predict that in the strongly-correlated limit the electronic bands in EuS_2 have a non-trivial topology, which results in sizable nearly-quantized values of the anomalous Hall conductivity (AHC) exhibited by the f-states. Remarkably, we find that the SHE in the system largely follows the behavior of the AHE owing to the strong majority character of the occupied f-states, while the OHE exhibits a very non-trivial behavior as a function of band filling, reaching a magnitude more than six times larger than that of the SHE. The detailed analysis we have carried out of the electronic structure in conjunction with Hall effects in the EuS_2 makes it possible to grasp the basic principles that can be used to turn rare-earth dichalcogenides into an an efficient source of orbital currents. Given a strong tendency of this class of materials to magnetism we thus propose that rare-earth dichalcogenides can occupy a unique place in the exotic niche of 2D magnetic materials with high potential for spintronics and orbitronics. Our manuscript is structured as follows: in Section II we provide computational details of our study. In Section III we present the results of our calculations and analysis, including a discussion, and we end with a brief conclusion in section IV.

II. COMPUTATIONAL DETAILS

Our first-principles calculations were performed using the film version of full-potential linearized augmented plane wave method [50], as implemented in the Jülich density functional theory (DFT) code FLEUR [51]. We used the Perdew-Burke-Ernzerhof approximation to the exchange-correlation potential [52]. The structure of the monolayer was relaxed so that residual forces are well below 0.001 eV/Å. For self-consistent calculations we used a 16×16 Monkhorst-Pack grid in the first Brillouin zone and a plane-wave cutoff of $4.1\,a_0^{-1}$, where a_0 is the Bohr radius. We set the angular momentum expansion of 10 and 8 for Eu and S atoms, respectively. The muffin-tin radii of Eu and S atoms were set to $2.8\,a_0$ and $1.94\,a_0$, respectively. Spin-orbit coupling (SOC) was included self-consistently within the second variation scheme for all calculations.

To treat the effect of strongly correlated electrons in the $4f$-shell of Eu we applied the GGA+U method within the self-consistent DFT cycle [53]. The on-site Coulomb interaction strength U applied to the Eu $4f$ states was varied from 0 eV to 6.7 eV, and the intra-atomic exchange interaction strength J was chosen to be 0.7 eV [53]. The optimized structure of H-EuS_2 is shown in Fig. 1 together with the definition of the axes. We first performed structural relaxations without U, which yielded a lattice constant of H-EuS_2 of 4.616 Å and a distance between the planes of Eu and S atoms along the z-axis of 1.1 Å. Adding a Coulomb repulsion strength of $U = 6.7$ eV modified the values of respective distances to 4.744 Å and 1.08 Å. All calculations were performed for the latter values of structural constants.

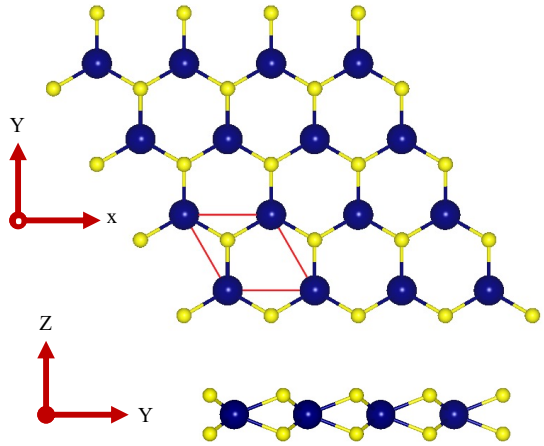

FIG. 1. Top and side view of the H-phase monolayer EuS_2. The dark blue balls and yellow balls represent Eu and S atoms, respectively. The definition of the axes is shown with arrows.

Transport calculations were performed for two values of U: 2.5 eV and 6.7 eV. The calculations of AHC, spin Hall conductivity (SHC), and orbital Hall conductivity (OHC) were performed according to expressions discussed below by exploiting the technique of Wannier interpolation [54, 55]. In order to do this, 36 maximally-localized Wannier functions were constructed out of the *ab-initio* electronic structure, by projecting the Bloch states onto p-states of S and f, d-states of Eu atoms, so as to reproduce the electronic structure in an energy window that contains all the states below the Fermi energy and enough number of states above the Fermi energy. Throughout this work we treat the system as an perpendicularly magnetized ferromagnet. For $U = 6.7$ eV the magnetic anisotropy energy was estimated to be of the order of 30 μeV favoring the out-of-plane direction of magnetization, while the ferromagnetic state was found to be 0.3 meV lower in energy than the row-wise antiferromagnetic state. We have to remark that these values may change upon changes in the Fermi energy in the system upon doping, which presents the main case of interest in this study (see discussion below).

III. RESULTS AND DISCUSSION

A. Electronic structure of EuS_2

We first discuss the electronic structure of EuS_2. We recall that consistent with Hund's first rule the intratomic exchange interaction arranges the electronic configuration of the half-filled Eu $4f$ shell in the $4f^7$ configuration, giving rise to a large magnetic moment of $6.95\,\mu_B$ – a value which is robust with respect to the correlation strength. This is significantly larger than the

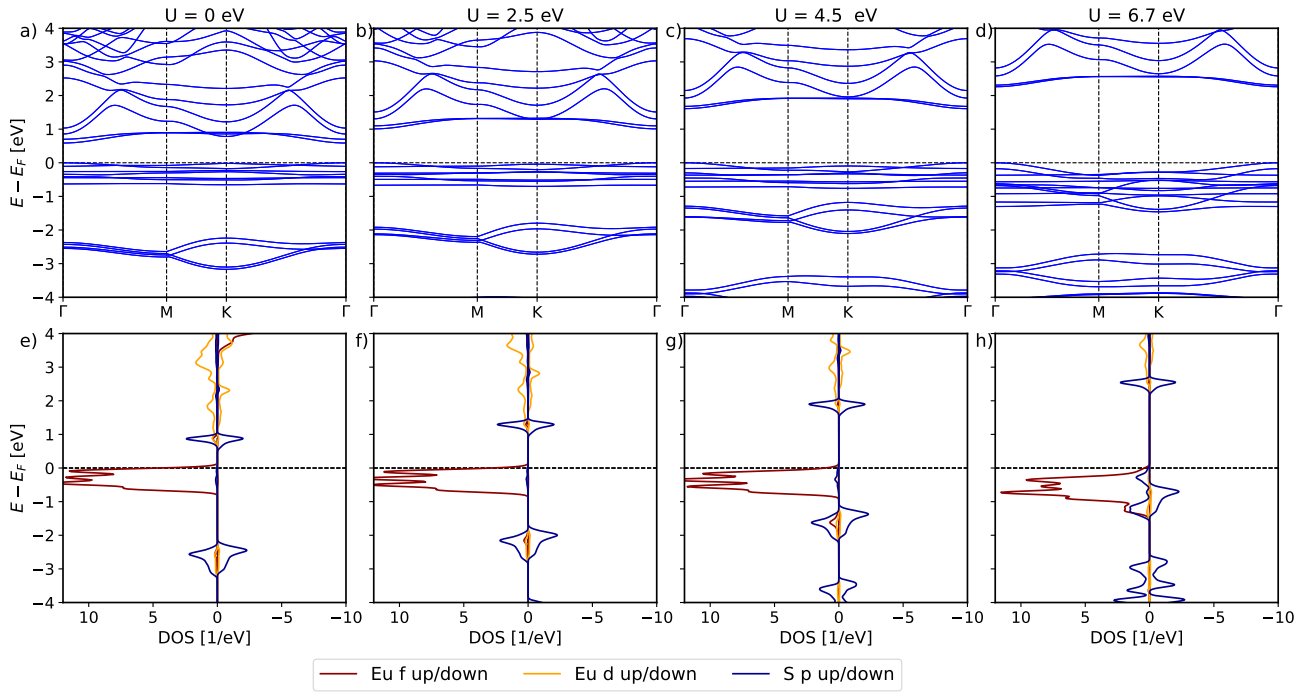

FIG. 2. Electronic structure of H-phase EuS_2 monolayer as a function of Coulomb repulsion strength U. In (a)-(d) the band structures are shown for $U = 0$, 2.5, 4.5 and 6.7 eV, respectively. In (e)-(h) the corresponding evolution of the spin-resolved density of states is shown. In (e)-(h) left and right parts of the figures correspond to the majority and minority spins, respectively, while the density of states of Eu-f, Eu-d and S-p states is shown with dark red, orange and blue thin lines, respectively. While the dominance of the majority Eu-f states at the Fermi level is evident, increasing U drives the hybridization of Eu-f-states with S-p states. This has drastic influence on the transport properties of the system, as discussed in the main text.

spin moments in other TMD materials, compare e.g. to Refs. [44, 48, 49]. In Fig. 2 we show the computed band structure of the system, (a-d), together with the densities of states (DOS), (e-h), for the values of U of 0 eV (a,e), 2.5 eV (b,f), 4.5 eV (c,g) and 6.7 eV (d,h). The quantitative features of the electronic structure of EuS_2 are similar irrespective of U: The highest occupied states are formed by the Eu $4f$ majority electrons. The position of the minority f-states varies from about +4 eV for $U = 0$ eV to about +10 eV for $U = 6.7$ eV, and we do not discuss these states further. The valence band maximum is positioned at the Γ point. We find p states of the chalcogen S atoms well separated and lying above and below the majority f states. Together with Eu f and d states the p states of S form bonding and antibonding states that have an energy separation of about 3.5 eV irrespective of the spin-channel. The lowest conduction band is relatively flat and it is formed by the states with primarily S-p character. The conduction band minimum is also positioned at the Γ point and EuS_2 monolayer exhibits a direct band gap of f-p transition. The higher conduction bands following the S-p band are formed by highly dispersing Eu $6s$ and $5d$ states. The localized occupied $4f$ states act as a repulsive scattering potential to the S-p electrons which moves bonding and antibonding S-p states in the majority and minority spin-channel to lower and higher energy, respectively. This introduces a small exchange splitting, visible in Fig. 2(a)-(d), and a magnetic moment of $-0.28\,\mu_B$ on S-atoms. The values of the orbital moments of Eu and S atoms are practically negligible.

Focusing on the $4f$ states, in the ground state, at $U = 0$ eV, the majority f-states are separated from the conduction S p-states by about 1 eV (direct band gap of 0.59 eV at Γ), see Fig. 2(a,e). Increasing U leads to an increase of the f-p gap without a change of dispersion, and the $4f$ states move down in energy closer to the occupied S p-valence states (or, alternatively, since the Fermi energy is fixed by the band edge of the majority $4f$ states, the S p-states move up in energy with respect to the f-states). At $U = 6.7$ eV this results in a p-f energy separation of about 3 eV at the Fermi energy (direct band gap of 2.27 eV at Γ), Fig. 2(d,h). This puts EuS_2 among the large band gap TMD semiconductors [56, 57]. On the other hand, increasing U drives the lower p-states into the region of majority f-states. In turn, this drives a strong hybridization between the p-, d- and f-states, which result in the orbital complexity and strong modifications that U brings to transport properties of the doped system which we discuss below. We conclude at this point that the EuS_2 monolayer is a ferromagnetic semiconductor with a direct band gap, whose value depends on the choice of U. The studied system can be turned into a half-metal upon replacing

Eu by e.g. Gd forming an $Eu_{1-x}Gd_xS_2$ layer.

B. Anomalous Hall effect in EuS_2

Next, we proceed to investigate the AHE in the system. Here, we focus on the intrinsic Berry curvature contribution to the AHC tensor [58]. To compute the Berry curvature from maximally-localized Wannier functions we first construct a tight-binding MLWFs Hamiltonian, and use the Wannier interpolation technique to efficiently evaluate the xy-component of the AHC, $\sigma_{\rm AH}$, as a Brillouin zone integral on a 300×300 mesh of k-points according to the expression:

$$\sigma_{\rm AH} = -\frac{e^2}{\hbar}\sum_n \int_{\rm BZ} \frac{d^2\boldsymbol{k}}{(2\pi)^2} f_{n\boldsymbol{k}}\,\Omega_{n\boldsymbol{k}}, \qquad (1)$$

with $f_{n\boldsymbol{k}}$ as the Fermi-Dirac distribution function, and the Berry curvature $\Omega_{n\mathbf{k}}$ of a state n at point $\boldsymbol{k}$ as given by

$$\Omega_{n\boldsymbol{k}} = 2\hbar^2 \sum_{n\neq m} \mathrm{Im}\left[\frac{\langle u_{n\boldsymbol{k}}|v_x|u_{m\boldsymbol{k}}\rangle\langle u_{m\boldsymbol{k}}|v_y|u_{n\boldsymbol{k}}\rangle}{(E_{n\boldsymbol{k}}-E_{m\boldsymbol{k}}+i\eta)^2}\right], \quad (2)$$

where $E_{n\boldsymbol{k}}$ is the energy of a Bloch state with lattice periodic part of Bloch wave function given by $u_{n\boldsymbol{k}}$, and v_i is the i'th Cartesian component of the velocity operator. For improving the convergence, we set $\eta = 25$ meV.

The results of our calculations of the AHC are summarized in Fig. 3(a) for the cases of $U = 2.5$ and 6.7 eV, of which we first discuss the former. The energy dependence of the AHC for $U = 2.5$ eV is shown with a dashed line in Fig. 3(a), where we observe that the AHC is non-zero only in a narrow window between -0.6 and $+0$ eV, and -3 to -2 eV. This corresponds to the upper region of majority f-states, and the region of occupied S p-states, respectively. The out-of-plane spin and orbital polarization of these states is shown in Figs. 4(a,b). We observe that the low lying p-states are slightly exchange split (by 50−100 meV), perfectly spin-polarized, and they display very strong orbital polarization, especially at the top and bottom of the group. This is consistent with the process of $p_x \pm p_y$ orbital polarization, confirmed by the DOS analysis (not shown), giving rise to non-trivial Chern numbers and a non-vanishing AHC in the region of these states [59]. By inspecting the region of f-states in Fig. 4(a,b) closer, we observe a formation of relatively large gaps among the groups of f-states, separated by the combined effect of crystal field and spin-orbit interaction. The topological nature of these gaps is predominantly trivial, i.e. the quantized value of the AHC within these gaps is topologically trivial, except for the case of the gap at about -0.4 eV, where the AHC is quantized to a value of $-1\,\frac{e^2}{h}$ (i.e. having a Chern number of -1). From the analysis of the orbital character of contributing states it is clear that this is the region where the overall change in the sign of orbital polarization of the states around the gap takes place. This change in the orbital polarization across the gap mediated by the spin-conserving part of spin-orbit interaction can be closely associated with the non-trivial AHC in this region [59].

At this point we would like to comment on the logic behind energy-resolved orbital polarization of the system for $U = 2.5$ eV. For this correlation strength, the Eu-f states are separated from the p-states of S atoms. The $4f$ electrons are localized, and experience a non-spherical potential exhibiting the point group symmetry of the Eu atom embedded into EuS_2 monolayer. Therefore, the development of the orbital moments is a result of a competition between Coulomb interaction, summarized under Hund's second rule, and the crystal field. We notice that our results still resemble Hund's second and third rule, Fig. 4(a,b). In the lower half of the $4f$-majority states, the orbital moment is opposite to the spin moment, while for the upper half of the $4f$ states the orbital moment is parallel to the spin moment, which results in a neglibile orbital moment when summed over all majority $4f$ states. For S-$4p$ states the situation is very different since the p-states are subject to a large band dispersion where crystal field effects dominate. For states along Γ-M the dispersion of the S p-states is rather small and Hund's third rule is obeyed since the orbital moments of the lower (upper) half of the bands is antiparallel (parallel) to the spin moments, but the strong crystal field associated with the band dispersion along the high-symmetry lines M-K-Γ makes Hund's third rule inapplicable. This violation becomes even more prominent for larger values of the correlation strength.

The effect of direct interaction between the p-states of S and f-states of Eu, taking place when we increase the correlation strength to $U = 6.7$ eV has a profound effect on the AHE. From the analysis of the DOS and spin-polarization of the states shown in Fig. 4(c) we observe that minority p-states are easily identifiable as they do not at all hybridize with the f-states of opposite spin. The hybridization of the majority p- and f-states is, on the other hand, drastic, which is evidenced by strong changes in the position and dispersion of the bands, as well as increased spread of Eu and S states over the region of almost 1.5 eV in energy for this spin channel. The resulting orbital complexity of hybridized states, visble in Fig. 4(c) has an amplifying effect on the overall magnitude of the AHC. In particular, close to quantized values of the AHC are achieved for the lower bands around -1.2 eV ($\sigma_{\rm AH} \approx +1\,\frac{e^2}{h}$ related to a global gap present there, crossed by minority-S states), a wide plateau around -0.6 eV (with $\sigma_{\rm AH} \approx -1\,\frac{e^2}{h}$, related to the non-trivial gap between three upper and five lower majority bands, separated by an "inactive" band at -0.55 eV), as well as a peak at -0.4 eV (with $\sigma_{\rm AH} \approx -2\,\frac{e^2}{h}$).

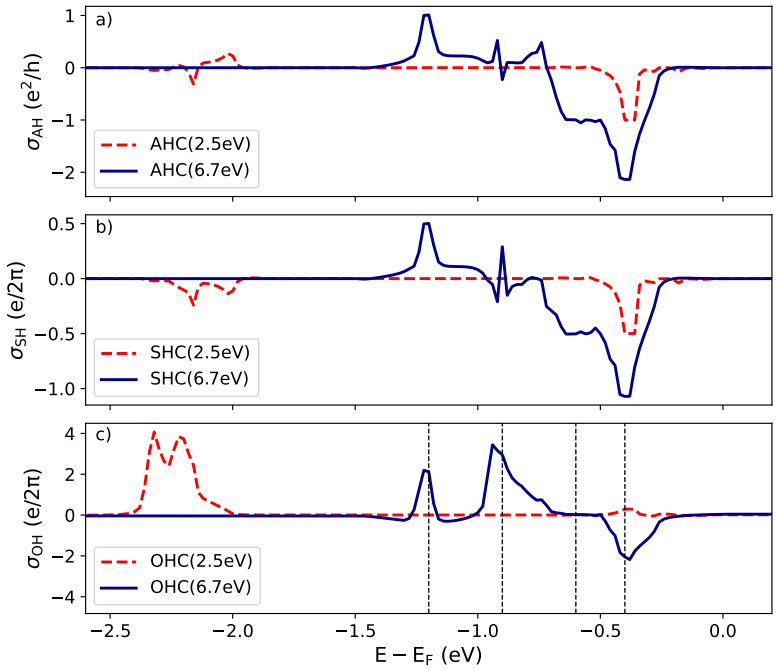

FIG. 3. Transport properties of monolayer EuS_2 as a function of band filling. (a) Anomalous Hall conductivity (AHC) $\sigma_{\rm AH}$, (b) spin Hall conductivity (SHC) $\sigma_{\rm SH}$, and (c) orbital Hall conductivity (OHC) $\sigma_{\rm OH}$, computed as a function of band filling in EuS_2 for $U = 2.5$ eV (red dashed line) and 6.7 eV (blue solid line). Vertical dashed lines in (c) are guides to the eye marking the position of energy at -1.2, -0.9, -0.6 and -0.4 eV. The influence of S-Eu hybridization at $U = 6.7$ eV is clearly visible in the plot: while in the case of weak hybridization at $U = 2.5$ eV the AHE and SHE in the system are suppressed, the combined effect of interacting S-p and Eu-f states on the overall magnitude and complex behavior of the AHE, SHE and OHE at $U = 6.7$ eV just below the Fermi energy is drastic.

C. Spin Hall effect in EuS_2

We now move on to the study of SHE and OHE in the system. While the SHE has been explicitly studied in group-VI dichalcogenides [11, 12], very recently, Canonico and co-workers investigated the orbital Hall effect in non-magnetic H-phase 2D TMDs MoS_2 and WS_2 [14, 16], addressing especially a question of quantization of the OHC within the electronic energy gaps, and corresponding emergence of the quantum orbital Hall insulating phase. The study of the OHE is a subject of general interest since the magnitude of the OHC can be often dominant over that of the SHC, which suggests systems with large OHE as potential platform for novel concepts in orbitronics [35, 60].

Motivated by these considerations, we proceed to explore the possibility that EuS_2 can host SHE and OHE. Following the established methodology [22, 61], we calculate the SHC and OHC, which mediates a generation of a transverse in-plane current of out-of-plane (spin or orbital) angular momentum in response to an applied electric field, according to the Kubo expression:

$$\sigma_{\rm OH/SH} = \frac{e}{\hbar}\sum_n \int \frac{d^2\boldsymbol{k}}{(2\pi)^2} f_{n_{\boldsymbol{k}}}\,\Omega^{J_z}_{n\boldsymbol{k}}, \tag{3}$$

where the so-called spin (orbital) Berry curvature reads as:

$$\Omega^{J_z}_{n\boldsymbol{k}} = 2\hbar^2 \sum_{m\neq n} {\rm Im}\left[\frac{\langle u_{n\boldsymbol{k}}|j_y^{J_z}|u_{m\boldsymbol{k}}\rangle\,\langle u_{m\boldsymbol{k}}|v_x|u_{m\boldsymbol{k}}\rangle}{(E_{n\boldsymbol{k}} - E_{m\boldsymbol{k}} + i\eta)^2}\right], \tag{4}$$

with $j_y^{J_z}$ as the spin ($J_z = S_z$, the z component of the spin operator) or orbital ($J_z = L_z$, the z component of the local angular momentum operator) current operator defined as $j_y^{J_z} = (v_y J_z + J_z v_y)/2$.

We first look at the SHE, presenting the results of the calculations in Fig. 3(b). For the case of $U = 2.5$ eV we find that for the f-states the SHC precisely follows the AHC as the band filling in varied. This is consistent with the picture of the spin angular momentum carried by the anomalous Hall current of fully spin-polarized f-bands in that energy region. The behavior of the SHC of S p-states at lower energies is more complicated, however, the consistently negative sign of the SHC can be understood from the sign reversal both in net spin-polarization as well as in the AHC at the top and at the bottom of the S-states. Remarkably, an almost perfect one-to-one correspondence between the energy dependence of the SHC and AHC still persists for a more complex case of $U = 6.7$ eV. This can be again understood taking into account pure spin character of f-states. The presence in that energy region of minority S-states, see Fig. 4(c-

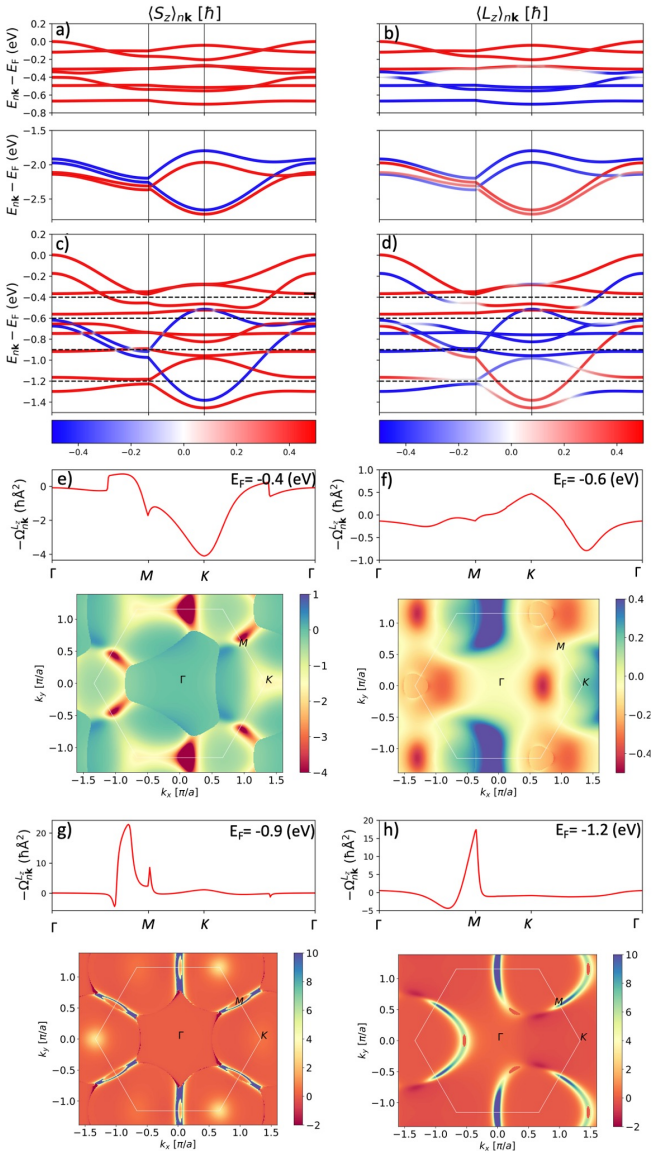

FIG. 4. Evolution of the out-of-plane spin, $\langle S_z\rangle_{n\mathbf{k}}$ (left panel: a,c), and orbital polarization, $\langle L_z\rangle_{n\mathbf{k}}$ (right panel: b,d), of occupied states in EuS_2. (a) The occupied spin-up f-states of Eu above $-0.8\,$eV (upper part), and S p-states in the region between -3 and $-1.5\,$eV (lower part) for the case of $U = 2.5\,$eV. Note that both groups of displayed states are isolated in energy from other states. (c) shows the hybridized group of occupied f and p-states for the case of $U = 6.7\,$eV which reside above $-1.5\,$eV. (b,d): Analogous to (a,c). The value scales are indicated by the color bars at the bottom in units of $\hbar$. Horizontal dashed lines in (c-d) are guides to the eye marking the position of energy at -1.2, -0.9, -0.6 and $-0.4\,$eV. (e-f) Distribution of the orbital Berry curvature along high symmetry lines for the indicated position of the Fermi energy, shown together with the distribution of the corresponding orbital Berry curvature in the Brillouin zone.

d), is the reason for a discrepancy in the shape of the SHC and AHC between -1.0 and $-0.6\,$eV, which can be explained by taking into account a small negative spin Hall signal that the minority S-states bring with them into that energy region.

D. Orbital Hall effect in EuS_2

Finally, we turn to the analysis of the OHE in the system. We present the results of our calculations of the OHC in Fig. 3(c). We first observe that in the "unhybridized" case of $U = 2.5\,$eV, the OHC of f-states is minimal, reaching in magnitude the SHC in the region around $-0.4\,$eV, where the AHE and SHE are present as well. Most remarkable is the gigantic OHE carried by the p-states of S atoms, positioned between -3 and $-2\,$eV, Fig. 4(b). The OHC in this region is almost one order of magnitude larger than the SHC or OHC of the f-states for this value of U. By inspecting the correlation between the electronic structure, orbital polarization and orbital Hall conductivity, we can identify a region of energy between -2.4 and $-2.1\,$eV as the dominant source of the OHE due to contributions coming from crossings among bands of different orbital character, clearly visible close to the M-point and the Γ-point in Fig. 4(b), as well as larger parts of the Brillouin zone where there is strong k-dependent exchange of orbital angular momentum among the oppositely-polarized bands, which is a direct consequence of k-dependent hybridization strength.

Upon increasing the value of U to $6.7\,$eV the complicated $p-d-f$ hybridization taking place among S and Eu atoms exerts a striking influence on the properties of the OHE of the $p-f$ group of states below the Fermi energy. This is reflected in a three to four times larger magnitude of the OHC as compared to the SHC observed in the region of majority f-states, Fig. 3(c), and, in contrast to expectations from oversimplifying band-filling arguments applied in the past to non-magnetic materials [19], a very non-trivial dependence of the OHC on the Fermi energy. At first, it is tempting to attribute the large computed OHC to S p-states, which promote a strong OHE already for smaller values of U without any need for aid from the side of f-orbitals. However, a closer analysis shows that this is not the case.

First, we take a look at the region of energy around $-1.2\,$eV, where the lowest of the peaks in the OHC appears [this energy value is indicated with dashed lines in Fig. 3(c) and Fig. 4(c-d)]. Here, the large peak in the OHC originates from an anticrossing among two strongly Eu-S hybridized bands [see also the corresponding DOS in Fig. 2(h)], positioned at that energy, where an exchange of the orbital polarization is particularly visible around the M-point. A very similar situation is encountered next to and directly at the M-point around $E_F = -0.9\,$eV, where the crucial role of the orbital angular momentum exchange and large values of the OHC displayed by the majority p-states become very apparent. The distribution of the orbital Berry curvature of occupied states up to the corresponding Fermi energy, shown in Fig. 4(g-h), confirms this picture. From the

k-space distribution of the orbital Berry curvature we observe that large OHE at these energies originates from sharp circular features centered around K′ points in the Brillouin zone.

Despite a sizable magnitude of the AHC and SHC in the region of energy between −0.7 and −0.5 eV [the value of −0.6 eV is marked with dashed lines in Fig. 3(c) and Fig. 4(c-d)], the OHC is suppressed there, which is quite unexpected. The reason for this is the absence of the k-dependent exchange of the orbital polarization among pairs of bands, which appear in this energy window. And although there is a crossing of positively and negatively orbitally polarized bands around −0.55 eV in the vicinity of the K-point, no hybridization or exchange of orbital angular momentum takes place there. The corresponding orbital Berry curvature for this Fermi energy, shown in Fig. 4(f), is overall more than one order of magnitude smaller than for the previously considered cases. This solidifies the k-dependent orbital polarization exchange as a driving force behind large OHE observed in the studied system at lower energies.

The scenario for the large OHC in the vicinity of −0.4 eV is different: here, it is the orbital exchange around M and K, taking place among pairs of bands well-separated in energy, i.e. the 2nd and 3rd bands when counting down from zero energy. While this gives rise to moderate negative values of the orbital Berry curvature over larger regions of the reciprocal space around K, smaller regions of reciprocal space around M and especially M′ contribute prominently to the overall sizeable OHC, Fig. 4(e). The negative sign of the OHC here, which cannot be achieved neither with p nor f-states separately (for lower U), emphasizes once more the importance of the p-f hybridization for the orbital Hall physics in EuS_2 in particular, and in rare earth dichalcogenides in general.

IV. DISCUSSION

The main motivation behind our work was the exploration of possible benefits that the combination of chalcogenides with f-elements in 2D geometry can bring. Here, we chose EuS_2 as a representative of this class of materials. One of the main strong points of this type of systems, besides a very prominent magnetism that f-electrons exhibit, is the strong spin-orbit interaction mediated by the f-states. This is a very robust and unique feature which is very difficult to achieve with other types of TMDs, where magnetism is much more fragile and the influence of structure on the nature of exchange-split bands is much stronger. Combined with the orbital complexity of f-states, robust magnetism has a potential to give rise to topologically non-trivial anomalous and spin Hall effects. While the strong localization of f-states naturally suppresses interatomic hybridization among atoms of f-species, the expectation is that the hybridization with highly dispersive p-states of chalcogenides will aid in promoting strong Hall effects, unachievable neither by pure f-system, nor by at best slighly magnetizated p-bands. Fostering a strong hybridization between f- and p-atoms thus presents a material challenge. At the same time, while it is known that even non-magnetic p-systems can host large orbital transport properties, a material system which exhibits very large anomalous, spin and orbital Hall effect at the same time, is not known so far. In this context, rare-earth dichalcogenides thus present an exciting platform for realization of pronounced transport phenomena of diverse nature.

With our work we attempt to initiate a focused research on discovery and characterization of rare-earth dichalcogenides, by showing that exiting properties listed above can be achieved in principle. In the course of our study of structural, electronic, magnetic and transport properties of EuS_2 from first principles we expectedly found that EuS_2 exhibits pronounced magnetism. We also found that this f-material gives rise to very strong Hall responses and hosts topologically non-trivial bands, despite strong correlation among electrons in the f-shell. We identified that the reason for this is a strong degree of $p-d-f$ hybridization among the Eu and S atoms, enhanced by stronger correlation effects owing to peculiar electronic structure of EuS_2. Effectively, the S-originated p-states and Eu f-states unite their efforts in enhancing each other's anomalous and spin Hall response. As a result of complex orbital hybridization among the latter states, the composite $p-f$ group of states also exhibits a very large orbital Hall effect, which is dominant over the SHE by about a factor of three. We identify k-dependent orbital exchange among pairs of hybridized bands as the major source and physical mechanism of large and non-trivial orbital Hall effect, which should be explored further as the possible governing force behind the large orbital Hall effect in magnetic materials in general.

Concerning the feasibility of experimental observation of the studied system, we have to remark that several compounds of Eu with chalcogenides are experimentally known in bulk, at interfaces and in thin films e.g. based on EuS [62–66], $EuSe_2$ [67] and $EuTe_2$ [68]. We thus believe that thin two-dimensional layers of EuS_2 can be naturally produced using for example exfoliation or molecular beam epitaxy. On the other hand, the general conclusions of our work are valid for the entire class of two-dimensional rare-earth dichalcogenides, marking them as an exciting platform for spin and orbital physics, and advancing our understanding of complex orbital transport manifestations of correlated magnetic two-dimensional materials.

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[1] A. Splendiani, L. Sun, Y. Zhang, T. Li, J. Kim, C.-Y. Chim, G. Galli, and F. Wang, Emerging photoluminescence in monolayer mos2, Nano Letters **10**, 1271 (2010), pMID: 20229981, https://doi.org/10.1021/nl903868w.

[2] H. R. Gutiérrez, N. Perea-López, A. L. Elías, A. Berkdemir, B. Wang, R. Lv, F. López-Urías, V. H. Crespi, H. Terrones, and M. Terrones, Extraordinary room-temperature photoluminescence in triangular ws2 monolayers, Nano Letters **13**, 3447 (2013), pMID: 23194096, https://doi.org/10.1021/nl3026357.

[3] P. Miró, M. Ghorbani-Asl, and T. Heine, Two dimensional materials beyond mos2: noble-transition-metal dichalcogenides., Angewandte Chemie **53 11**, 3015 (2014).

[4] C.-H. Lee, E. C. Silva, L. Calderin, M. A. T. Nguyen, M. J. Hollander, B. Bersch, T. E. Mallouk, and J. A. Robinson, Tungsten ditelluride: a layered semimetal, Scientific Reports **5**, 10013 (2015).

[5] S. Zhao, T. Hotta, T. Koretsune, K. Watanabe, T. Taniguchi, K. Sugawara, T. Takahashi, H. Shinohara, and R. Kitaura, Two-dimensional metallic nbs2: Growth, optical identification and transport properties, 2D Materials **3**, 025027 (2016).

[6] I. Guillamón, H. Suderow, J. G. Rodrigo, S. Vieira, P. Rodière, L. Cario, E. Navarro-Moratalla, C. Martí-Gastaldo, and E. Coronado, Chiral charge order in the superconductor 2h-tas2, New Journal of Physics **13**, 103020 (2011).

[7] Z. Y. Zhu, Y. C. Cheng, and U. Schwingenschlögl, Giant spin-orbit-induced spin splitting in two-dimensional transition-metal dichalcogenide semiconductors, Phys. Rev. B **84**, 153402 (2011).

[8] H.-R. Fuh, B. Yan, S. chun Wu, C. Felser, and C. Chang, Metal-insulator transition and the anomalous hall effect in the layered magnetic materials vs2 and vse2, New Journal of Physics **18**, 113038 (2016).

[9] K. F. Mak, K. L. McGill, J. Park, and P. L. McEuen, The valley hall effect in mos2 transistors, Science **344**, 1489–1492 (2014).

[10] X. Zhou, R.-w. Zhang, Z. Zhang, W. Feng, Y. Mokrousov, and Y. Yao, Sign-reversible valley-dependent berry phase effects in 2d valley-half-semiconductors, npj Computational Materials **7** (2021).

[11] W. Feng, Y. Yao, W. Zhu, J. Zhou, W. Yao, and D. Xiao, Intrinsic spin hall effect in monolayers of group-vi dichalcogenides: A first-principles study, Phys. Rev. B **86**, 165108 (2012).

[12] D. Xiao, G.-B. Liu, W. Feng, X. Xu, and W. Yao, Coupled spin and valley physics in monolayers of mos_2 and other group-vi dichalcogenides, Phys. Rev. Lett. **108**, 196802 (2012).

[13] T. P. Cysne, M. Costa, L. M. Canonico, M. B. Nardelli, R. Muniz, and T. G. Rappoport, Disentangling orbital and valley hall effects in bilayers of transition metal dichalcogenides, Physical Review Letters **126**, 10.1103/physrevlett.126.056601 (2021).

[14] L. M. Canonico, T. P. Cysne, T. G. Rappoport, and R. B. Muniz, Two-dimensional orbital hall insulators, Phys. Rev. B **101**, 075429 (2020).

[15] S. Bhowal and S. Satpathy, Intrinsic orbital and spin hall effects in monolayer transition metal dichalcogenides, Phys. Rev. B **102**, 035409 (2020).

[16] L. M. Canonico, T. P. Cysne, A. Molina-Sanchez, R. B. Muniz, and T. G. Rappoport, Orbital hall insulating phase in transition metal dichalcogenide monolayers, Phys. Rev. B **101**, 161409 (2020).

[17] Y. Liu, Y. Gao, S. Zhang, J. He, J. Yu, and Z. Liu, Valleytronics in transition metal dichalcogenides materials, Nano Research , 1 (2019).

[18] B. A. Bernevig, T. L. Hughes, and S.-C. Zhang, Orbitronics: The intrinsic orbital current in p-doped silicon, Phys. Rev. Lett. **95**, 066601 (2005).

[19] T. Tanaka, H. Kontani, M. Naito, T. Naito, D. S. Hirashima, K. Yamada, and J. Inoue, Intrinsic spin hall effect and orbital hall effect in $4d$ and $5d$ transition metals, Phys. Rev. B **77**, 165117 (2008).

[20] D. Jo, D. Go, and H.-W. Lee, Gigantic intrinsic orbital hall effects in weakly spin-orbit coupled metals, Phys. Rev. B **98**, 214405 (2018).

[21] H. Kontani, T. Tanaka, D. S. Hirashima, K. Yamada, and J. Inoue, Giant orbital hall effect in transition metals: Origin of large spin and anomalous hall effects, Phys. Rev. Lett. **102**, 016601 (2009).

[22] D. Go, D. Jo, C. Kim, and H.-W. Lee, Intrinsic spin and orbital hall effects from orbital texture, Phys. Rev. Lett. **121**, 086602 (2018).

[23] T. P. Cysne, S. Bhowal, G. Vignale, and T. G. Rappoport, Orbital hall effect in bilayer transition metal dichalcogenides: From the intra-atomic approximation to the orbital magnetic moment approach (2022), arXiv:2201.03491 [cond-mat.mes-hall].

[24] W.-Y. Shan, H.-Z. Lu, and D. Xiao, Spin hall effect in spin-valley coupled monolayers of transition metal dichalcogenides, Bulletin of the American Physical Society **2014** (2013).

[25] S. Bhowal and S. Satpathy, Electronic structure and anomalous hall effect in the ferromagnetic $3d$−$5d$ superlattice $srmno_3/sriro_3$, Phys. Rev. B **99**, 245145 (2019).

[26] S. Bhowal and S. Satpathy, Dirac nodal lines and large spin hall effect in the $6h$-perovskite iridate $ba_3tiir_2o_9$, Phys. Rev. B **100**, 115101 (2019).

[27] J.-Y. You, C. Chen, Z. Zhang, X.-L. Sheng, S. A. Yang, and G. Su, Two-dimensional weyl half-semimetal and tunable quantum anomalous hall effect, Phys. Rev. B **100**, 064408 (2019).

[28] J. Sinova, S. O. Valenzuela, J. Wunderlich, C. H. Back, and T. Jungwirth, Spin hall effects, Rev. Mod. Phys. **87**, 1213 (2015).

[29] S. Bhowal and S. Satpathy, Intrinsic orbital moment and prediction of a large orbital hall effect in two-dimensional transition metal dichalcogenides, Phys. Rev. B **101**, 121112 (2020).

[30] I. V. Tokatly, Orbital momentum hall effect in p-doped graphane, Phys. Rev. B **82**, 161404 (2010).

[31] S. Bhowal and G. Vignale, Orbital hall effect as an alternative to valley hall effect in gapped graphene, Phys. Rev. B **103**, 195309 (2021).

[32] D. Go and H.-W. Lee, Orbital torque: Torque generation by orbital current injection, Phys. Rev. Research **2**, 013177 (2020).

[33] S. Lee, M.-G. Kang, D. Go, D. Kim, J.-H. Kang, T. Lee, G.-H. Lee, J. Kang, N. J. Lee, Y. Mokrousov, S. Kim, K.-J. Kim, K.-J. Lee, and B.-G. Park, Efficient conversion of orbital hall current to spin current for spin-orbit torque switching, Communications Physics **4**, 1 (2021).

[34] D. Go, F. Freimuth, J.-P. Hanke, F. Xue, O. Gomonay, K.-J. Lee, S. Blügel, P. M. Haney, H.-W. Lee, and Y. Mokrousov, Theory of current-induced angular momentum transfer dynamics in spin-orbit coupled systems, Phys. Rev. Research **2**, 033401 (2020).

[35] D. Go, D. Jo, T. Gao, K. Ando, S. Blügel, H.-W. Lee, and Y. Mokrousov, Orbital rashba effect in a surface-oxidized cu film, Phys. Rev. B **103**, L121113 (2021).

[36] M. Gibertini, M. Koperski, A. Morpurgo, and K. Novoselov, Magnetic 2d materials and heterostructures, Nature nanotechnology **14**, 408—419 (2019).

[37] B. gai Zhai, J. Du, X. Li, C. Xia, and Z. Wei, Two-dimensional ferromagnetic materials and related van der waals heterostructures: a first-principle study, Journal of Semiconductors (2019).

[38] Q. Shao, P. Li, L. Liu, H. Yang, S. Fukami, A. Razavi, H. Wu, K. Wang, F. Freimuth, Y. Mokrousov, M. D. Stiles, S. Emori, A. Hoffmann, J. Åkerman, K. Roy, J.-P. Wang, S.-H. Yang, K. Garello, and W. Zhang, Roadmap of spin–orbit torques, IEEE Transactions on Magnetics **57**, 1 (2021).

[39] B. Huang, G. Clark, E. Navarro-Moratalla, D. R. Klein, R. Cheng, K. L. Seyler, D. Zhong, E. Schmidgall, M. A. McGuire, D. H. Cobden, and et al., Layer-dependent ferromagnetism in a van der waals crystal down to the monolayer limit, Nature **546**, 270–273 (2017).

[40] Y. Deng, Y. Yu, Y. Song, J. Zhang, N. Z. Wang, Z. Sun, Y. Yi, Y. Z. Wu, S. Wu, J. Zhu, and et al., Gate-tunable room-temperature ferromagnetism in two-dimensional fe3gete2, Nature **563**, 94–99 (2018).

[41] C. Gong, L. Li, Z. Li, H. Ji, A. Stern, Y. Xia, T. Cao, W. Bao, C. Wang, Y. Wang, and et al., Discovery of intrinsic ferromagnetism in two-dimensional van der waals crystals, Nature **546**, 265–269 (2017).

[42] F. Zhu, L. Zhang, X. Wang, F. J. dos Santos, J. Song, T. Mueller, K. Schmalzl, W. F. Schmidt, A. Ivanov, J. T. Park, J. Xu, J. Ma, S. Lounis, S. Blügel, Y. Mokrousov, Y. Su, and T. Brückel, Topological magnon insulators in two-dimensional van der waals ferromagnets crsite$_3$ and crgete$_3$: towards intrinsic gap-tunability (2021), arXiv:2107.03835 [cond-mat.str-el].

[43] H. Pan, Magnetic and electronic evolutions of hydrogenated vte2 monolayer under tension, Scientific Reports **4** (2014).

[44] Y. Ma, Y. Dai, M. Guo, C. Niu, Y. Zhu, and B. Huang, Evidence of the existence of magnetism in pristine vx2 monolayers (x = s, se) and their strain-induced tunable magnetic properties, ACS Nano **6**, 1695 (2012), pMID: 22264067, https://doi.org/10.1021/nn204667z.

[45] W. Chen, J. min Zhang, Y. zhuang Nie, Q. lin Xia, and G. hua Guo, Electronic structure and magnetism of mte2 (m = ti, v, cr, mn, fe, co and ni) monolayers, Journal of Magnetism and Magnetic Materials **508**, 166878 (2020).

[46] C. Wang, X. Zhou, Y. Pan, J. Qiao, X. Kong, C.-C. Kaun, and W. Ji, Layer and doping tunable ferromagnetic order in two-dimensional Crs$_2$ layers, Phys. Rev. B **97**, 245409 (2018).

[47] H. Y. Lv, W. J. Lu, D. F. Shao, Y. Liu, and Y. P. Sun, Strain-controlled switch between ferromagnetism and antiferromagnetism in $1t-CrX_2$ (x = Se, te) monolayers, Phys. Rev. B **92**, 214419 (2015).

[48] C. Ataca, H. Şahin, and S. Ciraci, Stable, single-layer mx2 transition-metal oxides and dichalcogenides in a honeycomb-like structure, The Journal of Physical Chemistry C **116**, 8983 (2012), https://doi.org/10.1021/jp212558p.

[49] M. Kan, S. Adhikari, and Q. Sun, Ferromagnetism in mnx2 (x = s, se) monolayers, Phys. Chem. Chem. Phys. **16**, 4990 (2014).

[50] E. Wimmer, H. Krakauer, M. Weinert, and A. J. Freeman, Full-potential self-consistent linearized-augmented-plane-wave method for calculating the electronic structure of molecules and surfaces: o$_2$ molecule, Phys. Rev. B **24**, 864 (1981).

[51] For the program description, see https://www.flapw.de.

[52] J. P. Perdew, K. Burke, and M. Ernzerhof, Generalized gradient approximation made simple, Phys. Rev. Lett. **77**, 3865 (1996).

[53] A. B. Shick, A. I. Liechtenstein, and W. E. Pickett, Implementation of the lda+u method using the full-potential linearized augmented plane-wave basis, Phys. Rev. B **60**, 10763 (1999).

[54] G. Pizzi, V. Vitale, R. Arita, S. Blügel, F. Freimuth, G. Géranton, M. Gibertini, D. Gresch, C. Johnson, T. Koretsune, and et al., Wannier90 as a community code: new features and applications, Journal of Physics: Condensed Matter **32**, 165902 (2020).

[55] F. Freimuth, Y. Mokrousov, D. Wortmann, S. Heinze, and S. Blügel, Maximally localized wannier functions within the flapw formalism, Phys. Rev. B **78**, 035120 (2008).

[56] H. Guo, N. Lu, L. Wang, X. Wu, and X. C. Zeng, Tuning electronic and magnetic properties of early transition-metal dichalcogenides via tensile strain, The Journal of Physical Chemistry C **118**, 7242 (2014), https://doi.org/10.1021/jp501734s.

[57] Y. Jiao, L. Zhou, F. Ma, G. Gao, L. Kou, J. Bell, S. Sanvito, and A. Du, Predicting single-layer technetium dichalcogenides (tcx2, x = s, se) with promising applications in photovoltaics and photocatalysis, ACS Applied Materials & Interfaces **8**, 5385 (2016), pMID: 26859697, https://doi.org/10.1021/acsami.5b12606.

[58] N. Nagaosa, J. Sinova, S. Onoda, A. H. MacDonald, and N. P. Ong, Anomalous hall effect, Rev. Mod. Phys. **82**, 1539 (2010).

[59] H. Zhang, F. Freimuth, G. Bihlmayer, M. Ležaić, S. Blügel, and Y. Mokrousov, Engineering quantum anomalous hall phases with orbital and spin degrees of freedom, Phys. Rev. B **87**, 205132 (2013).

[60] H. Kontani, T. Tanaka, D. S. Hirashima, K. Yamada, and J. Inoue, Giant intrinsic spin and orbital hall effects in

sr_2mo_4 (m = Ru, rh, mo), Phys. Rev. Lett. **100**, 096601 (2008).

[61] D. Go, D. Jo, H.-W. Lee, M. Kläui, and Y. Mokrousov, Orbitronics: Orbital currents in solids, EPL (Europhysics Letters) **135**, 37001 (2021).

[62] S. D. Pappas, P. Poulopoulos, B. Lewitz, A. Straub, A. Goschew, V. Kapaklis, F. Wilhelm, A. Rogalev, and P. Fumagalli, Direct evidence for significant spin-polarization of eus in co/eus multilayers at room temperature, Scientific Reports **3** (2013).

[63] P. Poulopoulos, A. Goschew, V. Kapaklis, M. Wolff, A. Delimitis, F. Wilhelm, A. Rogalev, S. D. Pappas, A. Straub, and P. Fumagalli, Induced spin-polarization of eus at room temperature in ni/eus multilayers, Applied Physics Letters **104**, 112411 (2014), https://doi.org/10.1063/1.4869210.

[64] S. M. J. Beer, A. Muriqi, P. Lindner, M. Winter, D. Rogalla, M. Nolan, A. Ney, J. Debus, and A. Devi, Ferromagnetic europium sulfide thin films: Influence of precursors on magneto-optical properties, Chemistry of Materials **34**, 152 (2022), https://doi.org/10.1021/acs.chemmater.1c02958.

[65] C. J. P. Smits, A. T. Filip, J. T. Kohlhepp, H. J. M. Swagten, B. Koopmans, and W. J. M. de Jonge, Magnetic and structural properties of eus for magnetic tunnel junction barriers, Journal of Applied Physics **95**, 7405 (2004), https://doi.org/10.1063/1.1682931.

[66] A. T. Filip, P. LeClair, C. J. P. Smits, J. T. Kohlhepp, H. J. M. Swagten, B. Koopmans, and W. J. M. de Jonge, Spin-injection device based on eus magnetic tunnel barriers, Applied Physics Letters **81**, 1815 (2002), https://doi.org/10.1063/1.1503406.

[67] J. A. Cowen, P. Michlin, J. Kraus, S. D. Mahanti, J. A. Aitken, and M. G. Kanatzidis, Euse2: A novel antiferromagnetic rare-earth polychalcogenide, Journal of Applied Physics **85**, 5381 (1999).

[68] J. Yin, C. Wu, L. Li, J. Yu, H. Sun, B. Shen, B. A. Frandsen, D.-X. Yao, and M. Wang, Large negative magnetoresistance in the antiferromagnetic rare-earth dichalcogenide $eute_2$, Phys. Rev. Materials **4**, 013405 (2020).