Chern insulating phases and thermoelectric properties of EuO/MgO(001) superlattices

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The topological and thermoelectric properties of (EuO)$_n$/(MgO)$_m$(001) superlattices (SLs) are explored using density functional theory calculations including a Hubbard U term together with Boltzmann transport theory. In (EuO)$_1$/(MgO)$_3$(001) SL at the lattice constant of MgO a sizable band gap of 0.51 eV is opened by spin-orbit coupling (SOC) due to a band inversion between occupied localized Eu 4$f$ and 5$d$ conduction electrons. This band inversion between bands of opposite parity is accompanied by a spin reorientation in the spin-texture along the contour of band crossing surrounding the Γ point and leaves a Chern insulator with $C = -1$, also confirmed by the single edge state. Moreover, this Chern insulating phase shows promising thermoelectric properties, e.g. a Seebeck coefficient between 400 and 800 $\mu$VK$^{-1}$. A similar SOC-induced band inversion takes place also in the ferromagnetic semimetallic (EuO)$_2$/(MgO)$_2$(001) SL. Despite the vanishing band gap, it leads to a substantial anomalous Hall conductivity with values up to $-1.04 e^2/h$ and somewhat lower thermoelectric properties. Both systems emphasize the relation between non-trivial topological bands and thermoelectricity also in systems with broken inversion symmetry.

I. INTRODUCTION

Recently topological insulators (TIs), that are insulating in the bulk, but have topologically protected conducting edge states with dissipationless charge current at the surface, have attracted a lot of attention in the field of condensed matter physics. Several TIs from the V-VI group, e.g. Bi$_2$Se$_3$, Bi$_2$Te$_3$, Sb$_2$Te$_3$ are at the same time promising thermoelectric (TE) materials that can convert heat into electricity. The connection and common characteristics between TI, in particular $Z_2$ TIs which preserve time-reversal symmetry (TRS), and TE such as heavy elements, narrow band gaps have been recently pointed out. In contrast to our knowledge Chern insulators – the TRS broken analogue of TIs – have received little attention concerning TE applications. Chern insulators are characterized by a non-zero Chern number in the absence of an external magnetic field. It is a significant challenge to realise robust Chern insulators. One strategy to achieve breaking of TRS is via doping of magnetic impurities into known topological insulators, such e.g. Mn-doped HgTe-, Cr-, Fe-doped Bi$_2$Te$_3$, Bi$_2$Se$_3$, Sb$_2$Te$_3$. Further realizations possibilities are 5$d$ transition metal atoms on graphene as well as OsCl$_2$. Transition metal oxides (TMO) with their rich functionality, resulting from the intricate interplay of spin, orbital and lattice degrees of freedom, have a greater tendency towards TRS breaking and larger band gaps compared to conventional $sp$ bonded systems and are thus an attractive class of materials to search for topologically non-trivial states. Intensive efforts have been directed at finding Chern insulators in TMO that host a honeycomb lattice, for which Haldane predicted a quantized anomalous Hall effect in his seminal work for spinless fermions. A buckled honeycomb lattice can be formed in (111)-oriented AXO$_3$ perovskite superlattices (SL) by two consecutive triangular X-layers as proposed by Xiao et al. Several realizations have been proposed, e.g. SrIrO$_3$ and LaAuO$_3$ bilayers, however, considering correlation effects results in an AFM ground state for SrIrO$_3$. In the 3$d$ series, e.g. in (LaXO$_3$)$_2$/(LaAlO$_3$)$_2$(111) SLs, LaMnO$_3$ was identified as a Chern insulator with a band gap of 150 meV when P321 symmetry is preserved, but the ground state is a trivial Mott insulator with Jahn-Teller (JT) distortion.

Further candidates for quantum anomalous Hall insulators (QAHI) are LaRuO$_3$ and LaOsO$_3$ as well as the metastable symmetric ferromagnetic cases of LaPdO$_3$, LaPtO$_3$ and LaTcO$_3$ honeycomb bilayers encased in LaAlO$_3$(111). Corundum-derived SL provide another realization of the honeycomb lattice. A systematic study of the 3$d$, 4$d$ and 5$d$ series of corundum-based honeycomb layers (X$_2$O$_3$)$_2$/(Al$_2$O$_3$)$_2$(0001) identified the metastable cases of $X =$ Tc, Pt as Chern insulators with $C = -2$ and $-1$ and band gaps of 54 and 59 meV, respectively.

Other lattice types proposed as candidate Chern insulators are e.g. rutile-derived heterostructures.
pyrochloride\textsuperscript{52}, as well as rocksalt-derived superlattices as EuO/CdO\textsuperscript{33} and EuO/GdN SL\textsuperscript{33}. The aim in the latter system is to combine heavy elements with large SOC in the two initially topologically trivial components in a quantum well (QW) structure, where SOC can induce a band inversion as in the HgTe/CdTe QW, where band inversion was originally predicted and observed\textsuperscript{33,34}. EuO is one of the few ferromagnetically (FM) ordered semiconductors\textsuperscript{35} with a Curie temperature ($T_C$) of 69 K. In EuO/CdO QW the band inversion takes place between the occupied Eu 4$f$ and the Cd 5s states\textsuperscript{33}, whereas in EuO/GdN it involves Eu 4$f$ and the Gd 5$d$ states\textsuperscript{33}. The small band-inversion induced band gap in the meV range is attributed to the large \(\Delta l = 3\) which suggests phonon mediation. Here we follow a different strategy: by combining EuO with the large band gap insulator MgO we achieve under particular strain conditions – the lattice constant of MgO (4.21 Å) – a band inversion in (EuO)$_1$/[(MgO)$_3$(001)] SL between Eu 4$f$ and 5$d$ states within the same component, while MgO merely plays the role of a spacer. Similarly, in both EuO/CdO and EuO/GdN the CI component, while MgO merely plays the role of a spacer.

Already Hicks and Dresselhaus\textsuperscript{33} proposed that the TE properties of materials can be improved in reduced dimensions as e.g. in QW. Experimentally, a giant Seebeck coefficient was reported in \(\delta\)-doped SrTiO$_3$ SLs\textsuperscript{34}. The confinement- and strain-induced enhancement of TE properties was recently addressed in LaNiO$_3$/LaAlO$_3$(001) SLs\textsuperscript{35-37} and SrXO$_3$/SrTiO$_3$(001) quantum wells\textsuperscript{35,36}, as well as other SrTiO$_3$-based SLs\textsuperscript{35,36}. For example in (LaNiO$_3$)$_1$/[(LaAlO$_3$)$_3$(001) \textsuperscript{35} the confinement- and strain-induced metal-to-insulator transition (MIT) at \(a_{\text{STO}}\) leads to enhanced in-plane power factor and high Seebeck coefficient. Here, we address in particular the implications of the topological Chern state in (EuO)$_1$/[(MgO)$_3$(001) QWs on the thermoelectric properties using Boltzmann transport theory and compare to the (EuO)$_2$/[(MgO)$_2$(001) case.

II. THEORETICAL METHODS

Density functional calculations were performed for (EuO)$_n$/[(MgO)$_m$(001) SLs with the projector augmented wave (PAW) method\textsuperscript{38} as implemented in the VASP\textsuperscript{53} code. The cutoff energy of the plane-waves was set to 500 eV. For the exchange-correlation functional we used the generalized gradient approximation (GGA) by Perdew, Burke and Enzerhof\textsuperscript{38}. A \(\Gamma\)-centered \(k\)-point grid of 16×16×8 were adopted in the self-consistent calculations employing the tetrahedron method\textsuperscript{52}. Static electronic correlation effects were taken into account within the GGA +\(U\) approach of Liechtenstein et al.\textsuperscript{52} formulation. Consistent with previous studies\textsuperscript{53,54}, an on-site Coulomb repulsion parameter of \(U=7.4\) eV and an exchange interaction parameter \(J=1.1\) eV were considered for the Eu 4$f$ states in order to describe correctly the experimentally reported band gap of 1.12 eV\textsuperscript{52} of bulk EuO: a GGA+\(U\) value of 1.13 eV is obtained for antiferromagnetic coupling as a first approximation to the paramagnetic state and 0.65 eV for the ferromagnetic case, corresponding to the low-temperature phase. The optimized bulk lattice constant of EuO with ferro- and antiferromagnetic arrangement within GGA+\(U\) is \(a=5.184\) Å and \(a=5.193\) Å, respectively, slightly higher than the experimental value of \(a=5.141\) Å\textsuperscript{53}. Similarly, for bulk MgO GGA yields a bulk lattice parameter of \(a=4.24\) Å, somewhat larger than the experimental lattice constant \(a=4.21\) Å\textsuperscript{53,54}. We note that within GGA the band gap of MgO is significantly underestimated (4.28 eV), compared to the experimental value of 7.83 eV\textsuperscript{57} and can be improved only by considering many body effects.\textsuperscript{58} Still since the GGA band gap is much larger than the one of the active material EuO, this underestimation is unlikely to influence the results reported here. The heterostructures were modeled at the
FIG. 3: GGA+$U$ band structures of ferromagnetic (EuO)$_n$/(MgO)$_m$ (001) at fixed lateral lattice constant of MgO and a) constrained or b) optimized out-of-plane lattice constant $c$ for $n = 1$, $m = 3$, as well as c) optimized $c$ for $n = 2$, $m = 2$. Majority and minority channels are shown in dark blue/light orange. The corresponding GGA+$U+SOC$ band structures are displayed in the bottom panels d-f).

FIG. 4: In a-b) GGA+$U+SOC$ band structures for FM (EuO)$_1$/(MgO)$_3$ (001) and (EuO)$_2$/(MgO)$_2$ (001) with magnetization along the [001]-direction as well as c-d) Berry curvatures along the same $k$-path. The corresponding anomalous Hall conductivities (AHC) $\sigma_{xy}$ in units of $e^2/h$ as a function of the chemical potential are displayed in e-f).
experimental lateral lattice constant of MgO and internal parameters were relaxed until the Hellmann-Feynman forces are less than 1 meV/Å, while the c lattice constant was either fixed at the value of bulk MgO or relaxed. In the case of (EuO)$_1$/(MgO)$_3$(001) the topologically non-trivial case was also explored using the all-electron full-potential linearized augmented plane wave (LAPW) method as implemented in the Wien2k code. In particular, the anomalous Hall conductivity (AHC) calculations were performed on a dense k-point mesh of 144×144×12 using the wannier90 code. The transport coefficients based on input from the DFT calculations are obtained within the constant relaxation time approximation using the BoltzTraP code.

III. RESULTS AND DISCUSSION:

A. GGA+U results for (EuO)$_n$/(MgO)$_m$(001) quantum wells

In this Section we discuss the electronic properties of the (EuO)$_n$/(MgO)$_m$(001) superlattices, referred to as (n,m) in the following. According to Hund’s rule, Eu$^{2+}$ exhibits a formal 4f$^7$ configuration with a closed shell and a large magnetic moment of $\sim 7.0$ $\mu_B$. The ferromagnetic state is the ground state. The GGA+U element- and orbitally resolved band structure and the spin-dependent projected density of states (DOS) of (EuO)$_1$/(MgO)$_3$(001) with c$\text{MgO}$ are shown in Fig. 2a and c. Just below the Fermi level the band structure is dominated by the narrow (bandwidth $\sim 2$ eV) half-filled Eu 4f bands, whereas the conduction bands are strongly dispersive, e.g. along M-Γ-X and of prevailing Eu 5d character (see Fig. 2b), respectively. Moreover, the top of the valence and bottom of the conduction band of this quantum well touch along Γ-Z, rendering the system semimetallic with predominant contribution of majority spin bands. The main effect of the c relaxation is the enhanced dispersion and overlap of conduction and valence bands along Γ-Z (cf. Fig. 3c). On the other hand, the band structure of (EuO)$_2$/(MgO)$_2$(001) with relaxed c (cf. Figs. 2b and 3b) bears some similarities to n = 1, m = 3 at the MgO c lattice constant, in particular, the touching flat conduction and valence bands along Γ-Z, however exhibits a much stronger overlap and hybridization between the Eu 4f and O 2p bands and a pronounced O 2p contribution along Γ-Z just below the Fermi level, visible also in the orbitally projected DOS in Figs. 2c and d.

B. Effect of spin-orbit coupling and topological analysis

Despite the similar features in the bandstructure, the effect of spin-orbit coupling is very distinct for the three systems. The corresponding band structures are displayed in Fig. 3i-f. While (EuO)$_1$/(MgO)$_3$(001) with relaxed c remains metallic with no pronounced rearrangement of bands, for (EuO)$_1$/(MgO)$_3$(001) at c = 2a$_{\text{MgO}}$ a significant band gap of 0.51 eV is opened for SOC with out-of-plane magnetization direction. Apparently, the degeneracy of the touching bands at the Fermi level is lifted giving rise to a band inversion along Γ-Z. The band inversion is present but the band gap is nearly vanishing for (EuO)$_2$/(MgO)$_2$(001) with relaxed c (see inset in Fig. 3i). In order to analyze the origin of the band rearrangement and inversion we plot in Fig. 4a and b the element and orbital projections on the band structure with SOC for (1,3) and (2,2). In contrast to the previously reported band inversion between Eu 4f and Cd 5s bands in EuO/CdO(001) or Eu 4f and Gd 5d states in EuO/GdN St[14], for (EuO)$_1$/(MgO)$_3$(001) at
\( c = 2a_{\text{MgO}} \) the band inversion takes place between the 4\( f \) and 5\( d \) states of Eu itself. The strong interaction of these bands of opposite parity and \( \Delta l = 3 \) leads to a substantial band gap opening. Interestingly this bears analogies with previous reports of bulk EuO under pressure, where fluctuations from the \((4f)^7(5d)^0\) to a \((4f)^8(5d)^1\) configuration were suggested in experimental\cite{72} and theoretical studies\cite{73,74}. Upon inclusion of SOC the band structure of \((\text{EuO})_2/(\text{MgO})_2(001)\) with relaxed \( c \) shows a reduced contribution of O 2\( p \) along \( \Gamma-Z \) and a similar in-
version of the topmost Eu 4f and lowest 5d band around $E_F$, though with a vanishing band gap. In contrast to the previously reported band inversion between Eu 4f and Cd 5s bands in EuO/CdO(001) [33] or Eu 4f and Gd 5d states in EuO/GdN SL [33], for (EuO)$_1$/(MgO)$_3$ (001) at $c = 2a_{\text{MgO}}$ the band inversion takes place between the 4f and 5d states of Eu itself. The strong interaction of these bands of opposite parity and $\Delta I = 3$ leads to a substantial band gap opening. Interestingly this bears analogies with previous reports of bulk EuO under pressure, where fluctuations from the $(4f)^7(5d)^0$ to a $(4f)^6(5d)^1$ configuration were suggested in experimental [33] and theoretical studies [53,54].

Upon inclusion of SOC the band structure of (EuO)$_2$/(MgO)$_2$(001) with relaxed c shows a reduced contribution of O 2p along Γ-Z and a similar inversion of the topmost Eu 4f and lowest 5d band around $E_F$, though with a vanishing band gap.

Having identified the origin of the band rearrangement and inversion for the two systems, we proceed to analyze the topological properties. The corresponding Berry curvature $\Omega(k)$ (cf. Fig. 3) for (1,3) exhibits strong negative peaks arising along the Γ-X and Γ-M′-Γ paths, whereas the contribution to the Berry curvature decreases and is flat along Γ-Z. The calculation of the anomalous Hall conductivity in Fig. 4 indicates the emergence of a broad plateau of $\sigma_{xy}$, rendering (EuO)$_1$/(MgO)$_3$(001) a Chern insulator with $C = -1$. As shown in Fig. 4, sharp peaks arise in the Berry curvature $\Omega(k)$ of (EuO)$_2$/(MgO)$_2$(001) at the avoided Eu 4f and 5d bands crossing along the M′-Γ and Z-R paths with values of 3000 and 8000 bohr$^{-2}$. For (EuO)$_2$/(MgO)$_2$(001) the Hall conductivity in Fig. 5 shows substantial, nearly quantized values (−1.04 e$^2$/h) caused by the non-trivial bands but the plateau is slightly shifted above $E_F$.

In Fig. 5a we plot the spin texture of the relevant bands of (1,3) (see Fig. 4). The occupied band exhibits only positive $s_z$ values throughout the whole BZ. In contrast, the out-of-plane spin component $s_z$ of the lower part of the unoccupied parabolic band is negative around Γ but reverses sign further away from the BZ center. This switching of spin orientation can be seen along the Γ-Z paths, whereas the contribution to the Berry curvature $\Omega(k)$ (cf. Fig. 4c) for (1,3) exhibits only positive values of $\Omega(k)$.

In summary, the effect of strain on the topological and thermoelectric properties of (EuO)$_n$/(MgO)$_m$(001) superlattices has been studied by DFT + U + SOC calculations in conjunction with the semi-classical Boltzmann transport theory. Combining two topologically trivial materials EuO and MgO in a QW structure results in a Chern insulating phase. Particularly, (EuO)$_1$/(MgO)$_3$(001) SL with lattice parameters constrained to the ones of MgO exhibits semimetallic behavior. The inclusion of SOC opens a large band gap of 0.51 eV due to a band inversion between Eu 5d and 4f bands. This mechanism is distinct to previously proposed systems such as EuO/CdO and EuO/GdN SL, where the band inversion takes place between bands of different elements in the two constituents: Eu 4f and Cd 5s or Gd 5d, respectively. The resulting Chern insulating phase with $C = -1$ shows a sign reversal of the out-of-plane spin components $s_z$ along the loop of band inversion around Γ and a single chiral edge state.

### IV. SUMMARY

In summary, the effect of strain on the topological and thermoelectric properties of (EuO)$_n$/(MgO)$_m$(001) superlattices has been studied by DFT + U + SOC calculations in conjunction with the semi-classical Boltzmann transport theory. Combining two topologically trivial materials EuO and MgO in a QW structure results in a Chern insulating phase. Particularly, (EuO)$_1$/(MgO)$_3$(001) SL with lattice parameters constrained to the ones of MgO exhibits semimetallic behavior. The inclusion of SOC opens a large band gap of 0.51 eV due to a band inversion between Eu 5d and 4f bands. This mechanism is distinct to previously proposed systems such as EuO/CdO and EuO/GdN SL, where the band inversion takes place between bands of different elements in the two constituents: Eu 4f and Cd 5s or Gd 5d, respectively. The resulting Chern insulating phase with $C = -1$ shows a sign reversal of the out-of-plane spin components $s_z$ along the loop of band inversion around Γ and a single chiral edge state.

### C. Thermoelectric properties

In the following, we investigate the thermoelectric properties of the (EuO)$_n$/(MgO)$_m$(001) SLs with and without optimized out-of-plane lattice constants $c$. A central quantity related to the TE efficiency is the figure of merit:

$$ZT = \frac{S^2 \sigma}{\kappa T}$$

where $S$ is the Seebeck coefficient, $\sigma$ the conductivity and $\kappa$ the thermal conductivity. Another related quantity is the power factor $PF = S^2 \sigma$. In Fig. 6 we plot $\sigma/\tau$, the Seebeck coefficient and $PF/\tau$ for the systems studied in Fig. 3 at two different temperatures, 300 and 600 K. While (EuO)$_1$/(MgO)$_3$(001) with $c = 8.4 \AA$ is a Chern insulator upon inclusion of SOC (cf. Fig. 6), the other two systems remain metallic or semimetallic.
SL but with a vanishing band gap. The resulting band rearrangement close to $E_F$ leads to sharp peaks of the Berry curvature at the avoided band-crossing along $Z$-$R$ and a plateau in the anomalous Hall conductivity above $E_F$ with a notable value of $-1.04 \, e^2/h$. Moreover, the $(\text{EuO})_1/(\text{MgO})_3(001)$ SL exhibits enhanced thermoelectric performance in terms of Seebeck coefficient of 400-800 $\mu$VK$^{-1}$ and $PF/\tau$ of 0.8-1.2·10$^{11}$W/K$^2$ms depending on temperature, driven by both the confinement and topological nature of the system. This establishes a link between topological and thermoelectric properties also for systems with broken inversion symmetry.
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