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**Abstract**: Perovskite oxide heterostructures have provided opportunities for new technologies and materials with novel properties. In particular, researchers have been interested in the magnetism and two-dimensional electron gases that form at the interface of many of these heterostructures. Often, these properties are due to polar discontinuities, but here we use first-principles calculations to examine a heterostructure whose elements, EuO and EuTiO<sub>3</sub>, are both non-polar, yet are still conductive due to oxygen vacancies. Furthermore, the free electrons at the interface of this heterostructure are predicted to be spin-polarized, opening up possibilities for future research and devices.

Keywords: perovskites; metal oxides; 2 dimensional electron gas; interfaces; magnetism; spintronics

## 1. Introduction

The discovery of the 2D electron gas (2DEG) at the interface of SrTiO<sub>3</sub> (STO) and LaAlO<sub>3</sub> (LAO) [1] sparked great research interest in the interfacial properties of perovskite oxide heterostructures. Shortly after this discovery, magnetism was predicted [2] and then observed [3,4] at the LAO/STO interface, a very unusual feature given that both bulk LAO and STO are nonmagnetic. However, questions remain about the exact nature of the magnetism at the interface of perovskite heterostructures. Some previous work suggested that interfacial conductivity and magnetism in LAO/STO may arise from different electrons within the interface layer [5], meaning that the mobile electrons primarily remain nonmagnetic.

The here addressed 2DEGs are of great importance to the rapidly developing field of spintronics [6]. Within this field, for example, spin-transfer torque devices use a spinpolarized current to manipulate magnetic layers of material, which has applications in the development of non-volatile RAM. Typically, however, these currents are only spinpolarized by exposure to magnetic fields [7]. It would therefore be of practical and scientific interest to find heterostructures whose interface contains electrons that are simultaneously spin-polarized and conducting.

A primary reason for the 2DEG of LAO/STO is a polar discontinuity at the interface [8]. Cubic perovskite oxides, with chemical formula ABO<sub>3</sub>, have A-type cations at the cube corners, B-type cations at the cube centers, and oxygen ions at the face centers which form octahedra around the B cations (see Figure 1). Along the (001) direction, the unit cell can be thought of as containing two atomic layers: AO and BO<sub>2</sub>. In some cases, these layers are charge-neutral, as in the case of STO; the SrO and TiO<sub>2</sub> layers are neutral since the Sr, Ti, and O ions have nominal charges +2, +4, and -2, respectively. In the case of LAO and many other perovskites, however, the ionization states of the atoms cause the layers to alternate in charge from +1 to -1, creating a polar material. In the bulk, there are infinitely many layers, so that all electric fields cancel out. On the other hand, if a few layers of a polar perovskite sit on top of a non-polar perovskite substrate, the resulting electric field configuration causes a monotonous variation in the electric potential with increasing thickness of the polar material. This situation has been dubbed the "polar catastrophe". To



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**Copyright:** © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). avoid this, once the number of layers of the polar material reaches a critical value, half a charge carrier must be transferred to the substrate, in which case the electric field alternates direction and the potential oscillates around some value but never diverges. In the case of an n-type interface, formed by connecting a TiO<sub>2</sub> from STO to a LaO layer from LAO, a two-dimensional electron gas is formed at the interface when the number of LAO unit cells reaches four. In a p-type interface, where an SrO layer from STO is connected to an AlO<sub>2</sub> layer from LAO, holes are transferred to the interface.



**Figure 1.** The ideal cubic perovskite structure of EuTiO<sub>3</sub>. Eu atoms are shown in green, Ti in blue, and O in red.

The carrier density within the 2DEG of LAO/STO found by experiments was shown to be much higher than what would be expected if the polar discontinuity was the only effect at play [9]. Further experiments showed that oxygen vacancies [10,11] and exchange of cations at the interface [12] also greatly contribute to the carrier density. Oxygen vacancies have two main effects: the introduction of free electrons, since these electrons are no longer tied up in bonds, and causing the vacancy-containing layers to be somewhat positively charged, since there is charge transfer between cations and oxygen ions in other layers due to bonding. The net result is that the newly free electrons are attracted to the positively charged surface, forming a 2DEG. We note that this effect does not require either of the materials to be polar.

In the case of LAO/STO, magnetism at the interface is most commonly explained by additional charge being introduced, for the reasons explained above, into the STO layers, filling the normally empty conduction band consisting of Ti-d orbitals [2]. A DFT study of this interface predicted that oxygen vacancies were essential to the ferromagnetic state in LAO/STO [5]. Later research concluded that this interfacial magnetism could be induced by depositing a thin layer of the antiferromagnetic perovskite EuTiO<sub>3</sub> at the interface of LAO and STO [13], or by sandwiching a thin layer of STO between GdTiO<sub>3</sub> layers [14]. However, the exact mechanism leading to the magnetism of the 2DEG in these cases is not fully understood.

Substrates other than STO were also considered in forming interfacial electron gases. The emergence of 2DEG was observed or predicted at the interface of KTaO<sub>3</sub> (KTO) with various oxide materials such as LaVO<sub>3</sub> [15], LaCrO<sub>3</sub> [16], TbScO3 [17], LaTiO<sub>3</sub> [18], and LaAlO<sub>3</sub> [19]. The formation of the 2DEG works rather differently in these heterostructures compared to the prototypical LAO/STO heterostructure. In these cases, both materials are polar. In KTO, the KO planes have nominal charge -1, while the TaO<sub>2</sub> planes have charge +1. In a material like LAO, on the other hand, the LaO planes have charge +1, while the AlO<sub>2</sub> planes have charge -1. This means that, even though both materials are polar, there is still a polar discontinuity at the interface, and a 2DEG forms. In some cases, like in KTO/LAO, the mobility was considerably greater than that of STO/LAO.

Furthermore, two-dimensional superconductivity was discovered at the interface of KTO and EuO and LaAlO<sub>3</sub> [20–22], as well as at the interface of STO/LAO. These discoveries were significant in that superconductivity rarely occurs in two-dimensional systems. It was even more significant that superconductivity and magnetism were observed to coexist in LAO/STO [23].

A study by Zhang et al. [24] found ferromagnetism in the 2DEG at the interface of EuO (EO) and KTaO<sub>3</sub> (KTO) using both experimental and first-principles methods. EO is a ferromagnetic face-centered cubic crystal with a basis consisting of one Eu atom at the origin and one O atom at the center of the unit cell. The EO crystal can be viewed as a stack of EuO layers where adjacent layers are separated by a distance equal to half the lattice constant. The ionization states of the atoms in EO are  $Eu^{2+}$  and  $O^{2-}$ ; hence, each EuO layer is assigned zero nominal charge, making the EuO stack of the layers non-polar. Similarly, KTO consists of an alternating stack of KO and TaO<sub>2</sub> layers. The ionization states of KTO atoms are  $K^+$ ,  $Ta^{5+}$ , and  $O^{2-}$ , giving the KO and  $TaO_2$  layers nominal charges of -1 and +1, respectively, and thus making KTO polar. In both the experimental and theoretical portions of Zhang et al.'s study [24], oxygen vacancies were present at the interface. The ferromagnetism of the interface was confirmed by anomalous Hall effect (AHE) measurements. However, in DFT calculations, ferromagnetism was only found at the EuO/TaO<sub>2</sub> interface, while the EuO/KO interface was nonmagnetic. The authors indicated that their calculations revealed a hybridization of Eu-3d and Ta-5d orbitals, allowing EO to spin-polarize the interfacial electrons.

In this work, we examine the electronic and magnetic properties at the interface of ferromagnetic EO on antiferromagnetic EuTiO<sub>3</sub> (ETO), with and without oxygen vacancies, using density functional theory. We consider two possible configurations of the heterostructure: in one case, the topmost TiO<sub>2</sub> layer in ETO connects to a EuO layer in EO, while in the other, the topmost EuO layer in ETO connects to a EuO layer in EO. In the absence of oxygen vacancies, the resulting heterostructures are shown to be semiconductors with bandgap values close to those in ETO and EO. In the case where there are oxygen vacancies, we predict that an electron gas forms at the interface. Furthermore, we predict that a significant portion of the mobile electrons within this gas are spin-polarized.

## 2. Methods

We investigate the electronic properties of a system consisting of up to four unit cells of EuO on top of EuTiO<sub>3</sub> (ETO) substrate. The substrate is modeled as eight unit cells of ETO along the (001) direction. Since the resulting heterostructure constitutes a two-dimensional system whereas the DFT calculations are carried out in three dimensions, a vacuum layer of about 12 Å is added along the (001) direction. ETO is a cubic perovskite with a lattice constant a = 3.905 Å [25]. However, in the ground state, ETO is antiferromagnetic [26]; to account for this magnetic order, the volume of the unit cell is doubled in order to accommodate different spin orientations on the Eu atoms. Hence, the a and b lattice constants of the heterostructure are set to  $a\sqrt{2} = 5.52$  Å. On the other hand, EuO has a face-centered cubic structure with a lattice constant of 5.15 Å [27], and it is a ferromagnetic semiconductor. The lattice mismatch between ETO and EO implies that layers of EO grown on an ETO substrate will be under a tensile stress, similar to, but smaller than the corresponding tensile stress in the case of the EO/KTO heterostructure.

We carried out the calculations by using density functional theory (DFT) as implemented in the Vienna Ab-initio Simulation Package (VASP) [28]. Perdew–Burke–Ernzerhof (PBE) exchange–correlation functional [29] was used within the generalized gradient approximation (GGA), and the interaction between the cores and valence electrons is described through projector-augmented wave pseudopotentials [30]. In Eu, the valence electrons are taken to be the 5s<sup>2</sup>, 5p<sup>6</sup>, 6s<sup>2</sup>, and 4f<sup>7</sup> electrons; in Ti, they are the 3p<sup>6</sup>, 4s<sup>2</sup>, and 3d<sup>2</sup> electrons, while in O they are the 2s<sup>2</sup> and 2p<sup>4</sup> electrons. The electronic wave function was expanded in plane waves up to a maximum wave vector corresponding to an energy cutoff of 520 eV. When calculating the electronic structure of the ETO and EuO crystals, the integration over the Brillouin zone was carried out by summing over a zone-centered  $8 \times 8 \times 8$  mesh of k-points. For calculations on the heterostructure, which is a two-dimensional system, a zone-centered  $8 \times 8 \times 1$  mesh is used. Due to the highly localized nature of the electrons in the 4f orbitals of Eu, an onsite Coulomb repulsion term, known as the Hubbard parameter U, is added. The addition of this term also improves the calculated values of the energy bandgaps in semiconductors; these values are generally underestimated in DFT calculations due to the self-interaction error. In this work, we took U – J = 8 eV for the 4f states in Eu, where J is the Hund's exchange parameter.

In the heterostructure, consisting of a few unit cells of EO on top of eight unit cells of ETO, the atomic positions are first relaxed until the force on each atom is less than 0.03 eV/Å. Since ETO is taken to be the substrate, the atomic positions in the first five unit cells are frozen as in the ETO crystal, while those in the top three unit cells of ETO, as well as those in the EO unit cells, are relaxed. In a similar fashion, we have also relaxed the atomic positions in the heterostructure in the presence of an oxygen vacancy, which was created in the top ETO unit cell at the interface with EO. The relaxed heterostructure interface with an O vacancy is shown in Figure 2.



**Figure 2.** The interface of the ETO/EO heterostructure with the O vacancy pointed out. Eu atoms are shown in green, Ti in blue, and O in red.

## 3. Results and Discussion

To begin with, we discuss the results of the DFT calculations on EuO (EO) and EuTiO<sub>3</sub> (ETO) crystals. If the onsite Coulomb repulsion is ignored, DFT calculations would indicate that EO is a metal, in disagreement with the experiment. This is not unusual since GGA calculations severely underestimate energy bandgaps in semiconductors. With the inclusion of a Hubbard term, our DFT calculations predict that EO is a ferromagnetic semiconductor and that each Eu ion possesses a magnetic moment of approximately 7.0  $\mu_B$ , where  $\mu_B$  is the Bohr magneton, in agreement with the predictions of Hund's rules applied to the seven 4f electrons in Eu ions. In the absence of spin-orbit coupling, we find an indirect energy bandgap of 1.14 eV; the inclusion of spin-orbit coupling causes a small reduction in the value of the bandgap to 1.02 eV. These values are in good agreement with the experimental value of 1.1 eV for the bandgap [31]. The valence band maximum occurs at the Brillouin zone center, while the conduction band minimum occurs at point X. Our DFT+U calculation yields a direct bandgap of 1.22 eV for the antiferromagnetic phase of ETO; this value is slightly diminished to 1.12 eV upon taking spin-orbit coupling into account. These values are in good agreement with experiments that report a bandgap close to 1 eV [32,33]. Due to the relatively small effect of spin-orbit coupling on the electronic properties, we ignore it in our study of the ETO/EO heterostructure.

We performed DFT calculations using eight unit cells of ETO as the substrate with 2, 3, or 4 unit cells of EO placed above. Viewed along the (001) direction, a unit cell of ETO has one EuO layer and one TiO<sub>2</sub> layer, whereas a unit cell of EO has two EuO layers. First, we

consider the heterostructure configuration whereby the topmost  $TiO_2$  layer in ETO connects to an EuO layer in EO. Relaxation of the atomic positions leads to very small changes in the separation between adjacent layers, except for the two lowermost EuO layers in EO (at the interface) and the two topmost EuO layers in EO (the surface layers). The distance between the two lowermost EuO layers in EO is 2.66 Å, while that between the two topmost EuO layers is 2.46 Å; in a EuO crystal, the separation between adjacent EuO layers along the (001) direction is 2.57 Å. The increase in the distance between the two EuO layers results from the presence of the adjacent  $TiO_2$  layer, while the presence of vacuum (or the lack of another EuO layer) above the topmost layer leads to a decrease in the distance between it and the EuO layer below it.

In Figure 3, we plot the density of states for spin-up and spin-down electrons in the case of the heterostructure with eight ETO and four EO unit cells without any oxygen vacancies. It is clear that there is a gap between the valence and conduction bands and that the density of states at the Fermi level is zero, indicating that the material remains a semiconductor. A gap was predicted regardless of the number of EO layers. For structures comprising two, three, or four EO unit cells on top of the ETO substrate, the calculated DFT+U bandgap values are respectively given by 1.07 eV, 1.04 eV, and 0.98 eV. This is expected since there is no polar discontinuity or other potential sources of charge carriers. We also predict that the magnetic orders of the Eu atoms remain the same in both materials. The Eu atoms within the EO block remain ferromagnetic, while those in the ETO block remain antiferromagnetic. We note that the calculated bandgaps of the heterostructures are consistently smaller than those in the ETO and EO crystals. This may result from the lattice mismatch between ETO and EO and the resulting distortion due to atomic position relaxation.



**Figure 3.** Density of states for the ETO/EO heterostructure, without vacancies, for the case where four unit cells of EO sit on top of an ETO substrate. Spin-up (down) density of states is plotted as positive (negative). The dashed line at 0 eV represents the Fermi energy.

The formation of a two-dimensional electron gas at the interface between EO and ETO is realized through the creation of oxygen vacancies near the ETO surface. This is achieved by the deposition of Eu atoms on the ETO surface in ultrahigh vacuum; the Eu atoms will uptake oxygen atoms from the ETO surface to form EuO layers, resulting in the formation of oxygen vacancies [34–36].

To simulate oxygen vacancies, we removed one O atom from the topmost  $TiO_2$  layer of ETO in the unit cell of the heterostructure. Since the heterostructure unit cell contains 16 EuTiO<sub>3</sub> formula units, the removal of one oxygen atom from the heterostructure unit cell corresponds to removing 0.06 oxygen atoms from one formula unit; in other words, we are here considering EO layers on top of EuTiO<sub>3-x</sub> layers, where x = 0.06.

In Figure 4, we show some of the atom- and layer-resolved densities of states calculated from the heterostructure containing four EO unit cells on top of eight ETO unit cells. The non-zero density at the Fermi level shows that the material is a metal. The vast majority of

the Fermi states come from Ti d-orbitals, indicating that conduction occurs mainly in the  $TiO_2$  layers of ETO. In each metallic  $TiO_2$  layer, the Fermi energy crosses the conduction band, indicating that electrons, rather than holes, are the charge carriers in the  $TiO_2$  layers. This also makes clear that the conductivity is not entirely limited to the topmost layer, with all eight  $TiO_2$  layers having some nonzero DOS at the Fermi level, although this DOS becomes vanishingly small toward the bottom unit cell.



**Figure 4.** Calculated densities of states for the heterostructure with an oxygen vacancy. (a) The density of states (DOS) for the overall heterostructure, plotted for each atom and the total. (b) Same data as the plot in (a) but zoomed-in near the Fermi level to show which atoms are responsible for conduction. (c) The Ti-d DOS near the Fermi level for each TiO<sub>2</sub> layer. The substrate, modeled as 8 ETO unit cells, has 8 EuO layers numbered 1, 3, ... 15 and 8 TiO<sub>2</sub> layers numbered 2, 4, ... 16.

In the layer-resolved DOS, the energy of the conduction band edge varies regarding its position within the heterostructure, which is a phenomenon known as band bending. In this case, the band edge decreases in energy as we move up toward the interface, indicating that there is an electric field pointing from the interface to the bottom of the unit cell. Electrons, in turn, are drawn to the interface, indicating that conduction should be fairly well localized to the interface, despite some free charges accumulating in other layers.

The total number of mobile electrons may be found by integrating the DOS from the bottom of the conduction band to the Fermi level. Carrying out this integration on the Ti-d orbitals in each layer reveals that there are, starting from the top  $TiO_2$  layer, 0.3632, 0.1176, 0.1760, 0.1395, 0.0405, 0.0118, 0.0031, and 0.0005 mobile electrons, respectively. This indicates that the largest proportion of conduction occurs in the top layer of  $TiO_2$ . Conduction falls by nearly an order of magnitude four layers away from the interface, indicating that the conducting region is highly two-dimensional. The number of mobile electrons in each layer is not monotonically decreasing, as we would expect from purely electronic considerations. However, this ignores the competing change in energy due to ionic reconfiguration. It is possible that this behavior is due to a phenomenon that is analogous to charge density waves in the Peierls picture [37], in which electronic and ionic deformation energy considerations compete. In this case, these effects would exponentially decay as we move away from the interface.

Within the uppermost layer, there are significantly more spin-up Ti-d electrons than spin-down, indicating that these mobile electrons are spin-polarized. The calculated total magnetic moment from electrons in the Ti-d orbitals in this layer was 0.274  $\mu_B$ ,

corresponding to 0.137  $\mu_B$  per Ti atom. There was also a small contribution from the Ti-p electrons that bumped up the total magnetic moment of the layer to 0.332  $\mu_B$ . If we again integrate from the bottom of the conduction band to the Fermi energy but subtract the spin-down electrons from the spin-up electrons, we can determine the magnetic moment of the free electrons. Carrying out this calculation gives a moment of 0.197  $\mu_B$  for the uppermost TiO<sub>2</sub> layer, showing that much of the magnetism of this layer results from the difference in spin-up and spin-down mobile electrons; a smaller contribution (0.135  $\mu_B$ ) results from electrons in filled bands. The moment of Ti electrons drops by nearly two orders of magnitude for the next lowest TiO layer.

We next consider the configuration where the topmost ETO layer is a EuO layer, which connects to another EuO layer in the EO block. The results of calculations in this case are rather similar to that of the previous case, in many respects. Again, the relaxation of the atomic positions leads to changes in the separation between EuO layers in EO similar to the previous case: the distance between the two EuO layers, in EO, near the interface is found to be 2.46 Å, while that between the two topmost EuO layers is 2.64 Å. We also find that the material is insulating in the absence of oxygen vacancies. For the cases where two, three, or four unit cells of EO sit on top of the ETO substrate, the calculated energy bandgaps are given by 0.83 eV, 0.85 eV, and 0.91 eV, respectively. Due to the fact that an EuO layer resides at the interface (at the top of the ETO block) in this heterostructure, the oxygen vacancy was taken from the EuO layer directly above the topmost TiO<sub>2</sub> layer. In the presence of an oxygen vacancy, the system becomes metallic; in this case, the layer-resolved density of states (DOS) for this material reveals that there is a larger DOS at the Fermi level closer to the interface, with Fermi DOS dropping to near zero at the lowest layers of ETO, and that most of the states at the Fermi energy level are derived from Ti-d orbitals.

However, there is some difference in the integrated DOS for this configuration. From top to bottom, the calculated total number of mobile Ti electrons in each TiO<sub>2</sub> layer was 0.2052, 0.2062, 0.2420, 0.1017, 0.0333, 0.0135, 0.0071, and 0.0029. This indicates that the third layer from the top is most conductive, which contrasts with the previous case and indicates that conduction is not as neatly confined to the interface. The magnetic moment for the topmost Ti electrons was less than half that of the TiO<sub>2</sub>-EuO case at 0.092  $\mu_B$ , while that of Ti electrons in the second highest TiO layer was 0.017  $\mu_B$ , showing that magnetism is also less well confined to the interface in this case.

In conclusion, we have presented predictions for the electronic properties of a previously unstudied perovskite heterostructure, EO/ETO. We have predicted that this material exhibits the property of having two-dimensional spin-polarized free electrons without exposure to magnetic fields. It remains to be seen whether spin-polarized currents within these heterostructures are well-suited to practical devices. It may also be the case that free charge carrier density and other properties may be further enhanced. These remaining questions leave the door open for expanded research on perovskite/EuO heterostructures. Future calculations and experiments could explore the effects of increasing the number of vacancies and varying their positions. Another tactic worth exploring would be to replace ETO with another transition metal perovskite. Of particular interest would be those perovskites containing 4d or 5d valence electrons, as their behavior may differ from a perovskite containing Ti, which has 3d valence electrons.

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