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# Highly Spin-Polarized Conducting State at the Interface between Nonmagnetic Band Insulators: $\text{LaAlO}_3/\text{FeS}_2$ (001)

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**Highly spin-polarized conducting state  
at the interface between non-magnetic band insulators:  $\text{LaAlO}_3/\text{FeS}_2$  (001)**

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**Abstract:**

First-principles density functional calculations demonstrate that a spin-polarized two-dimensional conducting state can be realized at the interface between two non-magnetic band insulators. The (001) surface of the diamagnetic insulator  $\text{FeS}_2$  (pyrite) supports a localized surface state deriving from Fe  $d$ -orbitals near the conduction band minimum. The deposition of a few unit cells of the polar perovskite oxide  $\text{LaAlO}_3$  leads to electron transfer into these surface bands, thereby creating a conducting interface. The occupation of these narrow bands leads to an exchange splitting between the spin sub-bands, yielding a highly spin-polarized conducting state distinct from the rest of the non-magnetic, insulating bulk. Such an interface presents intriguing possibilities for spintronics applications.

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With the ever approaching scaling and power consumption limit of current semiconductor device technology, the search is on for new materials systems which could form the basis of the next of generation of devices.[1] Going beyond traditional semiconductors to other materials, such as complex oxides[2] and transition metal sulfides[3,4], could lead to lower power consumption and better scalability by offering more functionality based on various magnetic and

electric degrees of freedom.[5] This is especially true for atomically engineered interfaces where properties can be found that even the bulk constituents do not possess.[6]

One prominent system is the two-dimensional electron gas (2DEG) formed at the (001) interface between two insulating perovskite oxides,  $\text{LaAlO}_3$  and  $\text{SrTiO}_3$ . [7] Due to  $\text{LaAlO}_3$  being polar, charge is transferred to the interface to eliminate the internal electric field, leading to a 2DEG above a certain critical thickness of  $\text{LaAlO}_3$ . [8,9] Tunable metallic properties of this interface are promising for potential applications. [10-14] In addition, magnetism [15] and superconductivity [16] have been discovered at this interface, suggesting further implications for nanoelectronics. [6]

A spin-polarized 2DEG is an exciting prospect for spintronics, where involvement of the spin degree of freedom broadens the spectrum of potential applications. [17] Several systems have been proposed to incorporate magnetism, e.g. replacing  $\text{LaAlO}_3$  with the strongly correlated oxide  $\text{LaVO}_3$ , [18] embedding a  $\text{LaO}$  monolayer in  $\text{SrMnO}_3$ , [19] and exploiting the ferromagnetism of  $\text{EuO}$ . [20,21] These interfaces inherit magnetic properties from the constituent materials, either through magnetic order or their tendency toward strong correlations.

We propose a different approach to create a spin-polarized 2DEG: magnetism is induced at the interface between two non-magnetic insulators due to charge-transfer-driven exchange splitting of the interface states. Such an interface can be realized by pairing  $\text{LaAlO}_3$  with the diamagnetic band insulator  $\text{FeS}_2$ , commonly known as pyrite.  $\text{FeS}_2$  begins a series of pyrite-structure disulfides covering the late half of the  $3d$  elements all the way to  $\text{ZnS}_2$ , each displaying properties distinct from its neighbors. [22] In particular,  $\text{CoS}_2$  has one more  $d$  electron per formula unit than  $\text{FeS}_2$ , making it an itinerant ferromagnetic metal. Changing this charge through alloying of  $\text{CoS}_2$  and  $\text{FeS}_2$  allows tuning of the magnetic and transport properties. [3,23] This suggests that

by electron doping of a pure FeS<sub>2</sub> surface through heterostructuring with polar LaAlO<sub>3</sub> both conductivity and magnetism might exist at the same interface.

We present here results of first-principles density functional theory (DFT) calculations of LaAlO<sub>3</sub>/FeS<sub>2</sub> (001) interfaces that confirm the conducting and ferromagnetic behaviors at this interface. These properties are confined to the interface due to native surface/interface states of FeS<sub>2</sub> which are susceptible to Stoner exchange splitting when occupied, leading to itinerant ferromagnetism and substantial spin polarization.

DFT calculations are performed using the plane-wave pseudopotential method implemented in the Quantum ESPRESSO package.[24] A plane-wave cutoff energy of 400 eV and a generalized-gradient approximation (GGA)[25] were used in all calculations. Atomic relaxations were converged using a 4×4×1 Monkhorst-Pack  $k$ -point mesh, Gaussian broadening of 0.1 eV and force cutoff of 20 meV/Å. The resulting structures were used in subsequent frozen-lattice self-consistent calculations using a 10×10×1  $k$ -point mesh and broadening of 0.02 eV to refine the electronic density. Subsequent non-self-consistent calculations on a 48×48×1  $k$ -point mesh were performed to extract  $k_{\parallel}$ -resolved local density of states (LDOS) with 7 meV broadening.

Bulk FeS<sub>2</sub> has a quasi-rocksalt cubic structure consisting of Fe<sup>2+</sup> at the face centers and S<sub>2</sub><sup>2-</sup> dimers centered at the cube corners alternately aligned along the various body-diagonal axes, resulting in space group  $Pa\bar{3}$ . Calculations yield a cubic lattice constant of  $a = 5.410$  Å and a S<sub>2</sub><sup>2-</sup> bond length of  $d = 2.194$  Å, in agreement with previous calculations [26-28] and experiments.[29]

We study three heterostructure systems, shown in Fig. 1. In all cases the in-plane lattice parameter is fixed to that calculated for bulk FeS<sub>2</sub> to mimic epitaxial growth on a single crystal or well-relaxed film. The vertical supercell size is  $13a = 70.33$  Å. First we study the slab consisting

of 5 stoichiometric (001) layers of  $\text{FeS}_2$  embedded in vacuum (see Fig. 1a).[30] Other surface terminations are energetically unfavorable, making (001) an ideal cleavage plane for single crystals resulting in flat, atomically stepped, terraces up to a few hundred nm wide.[31] Atomic relaxation does not introduce dramatic changes to the structure with respect to the bulk, consistent with previous calculations [32,33] and experimental data. [31,34]

In bulk,  $\text{Fe}^{2+}$  cations are 6-fold coordinated by sulfur. The crystal field splits the  $3d$  manifold into a low-lying  $t_{2g}$  triplet and a higher energy  $e_g$  doublet. This splitting is large enough that the zero-spin state is favored with 6 electrons in the  $t_{2g}$  orbitals, leaving the  $e_g$  orbitals above the highly dispersive S  $3p$  states that form the conduction band minimum. This is evident from the LDOS of the bulk  $\text{FeS}_2$  layer in Fig. 2a. On the (001) surface  $\text{Fe}^{2+}$  cations are only 5-fold coordinated, modifying the crystal field environment of the Fe- $3d$  states. The  $e_g$  doublet is split and the  $t_{2g}$  states are split into a low singlet and a higher doublet. These split levels alone do not close the gap, leaving 6 spin-paired electrons in the “ $t_{2g}$ ” sector of the manifold. Since this change in splitting is localized at the surface, however, the high-lying levels of the “ $t_{2g}$ ” triplet and the low-lying member of the “ $e_g$ ” doublet constitute surface states near the top of the valence band and bottom of the conduction band, respectively.

These surface states are seen in Fig. 2a as peaks at around  $E_F \pm 0.4$  in the LDOS on  $\text{FeS}_2$ -1 which are not present in the bulk DOS, but quickly decay into the sub-surface layers. (For gapped systems the Fermi level,  $E_F$ , is at the center of the band gap.) The decay of the conduction band surface states are also seen in the  $k_{\parallel}$ - and layer-resolved LDOS plotted in Figs. 3a-c at  $E_F + 0.4$  eV. The narrow energy contours correspond to cuts through a two-dimensional band structure, demonstrating a decrease in intensity when moving from the surface (Fig.3a) to the bulk (Fig.3c). The circles around the  $\Gamma$  point correspond to cuts through the dispersive S  $3p$

states.

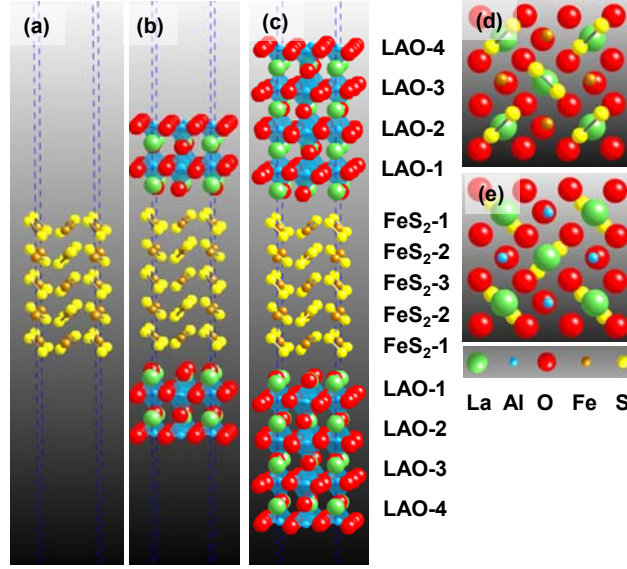


FIG 1. Atomic structures of the three systems studied: (a) FeS<sub>2</sub> slab consisting of five (001) atomic layers; (b,c) symmetric heterostructures with the FeS<sub>2</sub> slab covered by 2 (b) and 4 (c) u.c. LaAlO<sub>3</sub> films; (d,e) bottom (d) and top (e) views of the first few monolayers near the interface.

Next we study the LaAlO<sub>3</sub>/FeS<sub>2</sub> (001) interface. Bulk LaAlO<sub>3</sub> deviates from the perfect cubic perovskite structure by tilts and rotations of the oxygen octahedra around the Al sites, resulting in space group  $R\bar{3}c$ . Our GGA calculations of the bulk  $R\bar{3}c$  structure reveal a volume consistent with a cubic perovskite lattice parameter  $a_{cp} = 3.817$  Å. Epitaxial matching with the pyrite structure requires a  $\sqrt{2} \times \sqrt{2}$  in-plane doubling of the pseudocubic perovskite cell with a 45° rotation around the pseudocubic [001] direction, leading to an effective in-plane lattice constant of  $\sqrt{2}a_{cp} = 5.398$  Å. Matching to the FeS<sub>2</sub> lattice leads to -0.2% tensile strain, and calculations of bulk LaAlO<sub>3</sub> for this strain state reveal a C2/c structure, consistent with previous calculations.[35]

Using this C2/c structure we construct the heterostructures by adding 2 unit cell (u.c.) and 4 u.c. LaAlO<sub>3</sub> layers to the FeS<sub>2</sub> slab, as shown in Figs. 1b and 1c, respectively. LaAlO<sub>3</sub> films are

stoichiometric with LaO termination at the interface with FeS<sub>2</sub> and AlO<sub>2</sub> termination with vacuum. The LaO interface termination, with La<sup>3+</sup> above the center of the S<sub>2</sub><sup>2-</sup> dimers and O<sup>2-</sup> above the Fe<sup>2+</sup> sites, is a natural extension of the rock-salt-like ionic structure of the FeS<sub>2</sub> surface (Figs. 1d-e). Each supercell is inversion symmetric, eliminating any electric field in the vacuum regions. Supercells are sufficiently large to minimize interactions across the vacuum. The structures are then fully relaxed, resulting in layer-by-layer polar distortions (see Fig. S1 in the supplementary materials) due to internal electric fields as was found for similar systems.[9]

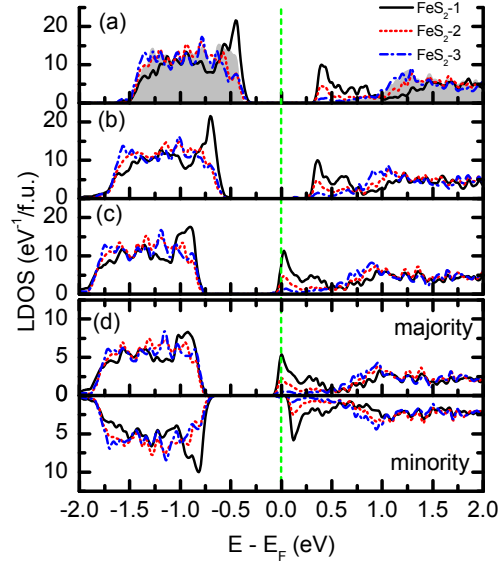


FIG 2. LDOS projected onto layers FeS<sub>2</sub>-1 through FeS<sub>2</sub>-3 (see Fig. 1) for a FeS<sub>2</sub> slab surrounded by (a) vacuum, (b) 2 u.c. LaAlO<sub>3</sub> and (c-d) 4 u.c. LaAlO<sub>3</sub>, as follows from non-spin polarized (c) and spin-polarized (d) calculations. The vertical dashed line indicates  $E_F$ . In (a) the filled curve is the total DOS of bulk FeS<sub>2</sub>.

The 2 u.c. LaAlO<sub>3</sub> system maintains a small, but true, band gap and thus remains insulating. Nevertheless since the electric field in the LaAlO<sub>3</sub> has decreased the overall band gap, the sur-

face/interface states at the bottom of the conduction band of FeS<sub>2</sub> are closer to  $E_F$  than those for the FeS<sub>2</sub> slab (Fig. 2a). (See also Fig. S2a in the supplementary materials.) This tendency persists with increasing LaAlO<sub>3</sub> thickness, and for the 4 u.c. LaAlO<sub>3</sub> heterostructure we find the overall band gap has closed, leaving  $E_F$  within the conduction band of FeS<sub>2</sub>, thus indicating metallicity of the interface (see Fig. 2c). (See also Fig. S2b in the supplementary materials.) This behavior is consistent with the charge transfer mechanism known for the well-studied LaAlO<sub>3</sub>/SrTiO<sub>3</sub> system.[9,36,37] The charge transfer for amounts to  $\sim 0.16$  electrons/interface Fe. This is consistent with the LaAlO<sub>3</sub>/SrTiO<sub>3</sub> system where, above a critical thickness of LaAlO<sub>3</sub>, electron transfer approaches 0.5 electrons in the limit of large LaAlO<sub>3</sub> thickness.[37]

The transferred electrons are almost entirely accommodated into the surface/interface states of FeS<sub>2</sub>. This is seen from the  $k_{\parallel}$ -resolved LDOS plotted in Figs. 3d-f, where the narrow contours correspond to the Fermi surface of this conducting interface, which are similar to the bare surface states in Figs. 3a-c.



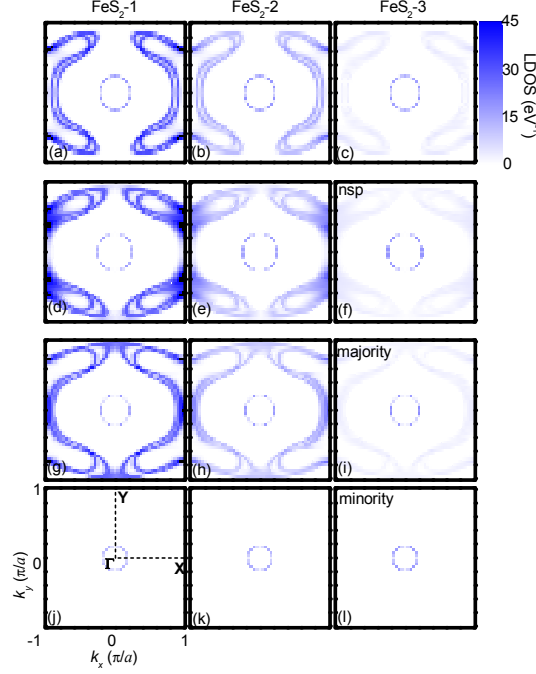


FIG 3.  $k_{\parallel}$ -resolved LDOS projected onto layers FeS<sub>2</sub>-1 through -3 (see Fig. 1) for a FeS<sub>2</sub> slab,  $E = E_F + 0.4$  eV (a-c) and LaAlO<sub>3</sub>(4 u.c.)/FeS<sub>2</sub> heterostructure,  $E = E_F$  (d-l). Results of non-spin-polarized (d-f) and spin-polarized calculations for majority (g-i) and minority spin (j-l) are shown.

The above calculations assumed no spin polarization. This constraint results in a large peak in the non-spin polarized LDOS at  $E_F$  on the interface in the 4 u.c. LaAlO<sub>3</sub> heterostructure (Fig. 3c). This suggests that exchange splitting of the spin bands might reduce electron energy,[38,39] and spin-polarized calculations confirm this prediction. Fig. 4 shows the spin density profile revealing that the magnetic moment comes mostly from the Fe sites in the FeS<sub>2</sub>-1 layer, whereas the magnetization in the rest of the structure is negligible. The induced moment is  $0.13 \mu_B$  per interface Fe, which is remarkably consistent with what is found experimentally for bulk Fe<sub>1-x</sub>Co<sub>x</sub>S<sub>2</sub> with  $x = 0.16$ , [22] corresponding to the charge transfer of  $0.16e$  found in our interface calculations. Spin-polarized calculations for the FeS<sub>2</sub>-vacuum slab and the heterostructure with 2

u.c. of  $\text{LaAlO}_3$ , however, do not reveal any magnetization, consistent with zero charge transfer.

As seen from Fig. 2d, the exchange splitting of the surface/interface states is 0.11 eV. This completely splits the Fe- $d$  states making the system nearly half-metallic with Fermi-level LDOS dominated by the majority-spin states. The spin- and  $k_{\parallel}$ -resolved LDOS in  $\text{FeS}_2$  are plotted in Figs. 3g-l. The majority-spin LDOS (Figs. 3g-i) looks similar to those for the non-spin polarized interface states. The minority-spin LDOS (Figs. 3j-l) displays only a 2-dimensional electron pocket, corresponding to the dispersive S  $3p$  states.

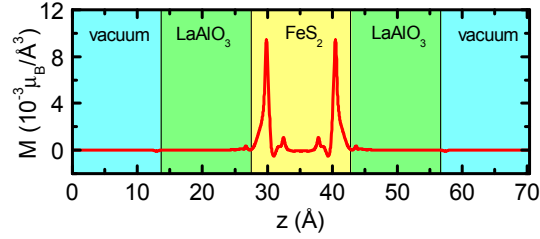


FIG 4. Distribution of magnetization,  $M$ , in the 4 u.c. heterostructure averaged over the plane parallel to the layers.

The appearance of exchange splitting of the interface states is consistent with the Stoner model for itinerant ferromagnetism.[38] This model begins with the non-magnetic DOS,  $\rho(\epsilon)$ , and transfers electrons from minority- to majority-spin states giving rise to a magnetic moment  $m$ . Lowering in energy occurs due to the reduced Coulomb interaction, characterized by the parameter  $I$ , between electrons occupying the same orbital. This competes with an increase in the overall kinetic, or “band”, energy of the system. If the condition  $I\rho(\epsilon_F) > 1$  is satisfied, then a stable magnetic moment is present, given by the relation  $\Delta = Im$ , where  $\Delta$  is the exchange splitting between spin bands. Taking  $m = 0.13 \mu_B/\text{Fe}$  and  $\Delta = 0.11$  eV from the LDOS in Fig. 2d we find an exchange parameter  $I = 0.84$  eV. This is consistent with first-principles calculations of  $I$

discussed in the supplementary material, as well as previous calculations[40] and values derived from experiments for Fe-containing systems.[41] In addition, previous DFT calculations of bulk (Fe,Co)S<sub>2</sub> alloys also reproduce quite well experimental trends of magnetic moment.[3] These facts indicate that our results do not suffer from incomplete account of electron correlations.

In conclusion we have predicted a conducting ferromagnetic interface between two non-magnetic band insulators, LaAlO<sub>3</sub> and FeS<sub>2</sub>. The polar nature of the LaAlO<sub>3</sub> (001) layer supports charge transfer to a localized surface/interface state formed by Fe *d*-orbitals at the conduction band minimum of FeS<sub>2</sub>. This nearly half-metallic interface may be interesting for spintronics applications.

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