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Conventionally, magnetic ordering in solids is associated with atoms with partly occupied $3d$ or $5f$ shells. There, large exchange energy $J$ results in the high-spin configuration of individual atoms. Coupling of these magnetic moments depends strongly on the material in question. In the metallic band picture of free electrons, ferromagnetic coupling is favored if the density of states at the Fermi level, $D(E_F)$, is high enough. In this case, the exchange energy gained by spin-polarizing the carriers is larger than their corresponding kinetic energy increase. This is known as the Stoner criterion, $JD(E_F) > 1$.

However, high density of states at the Fermi level and high exchange interaction are not restricted to these shells only. Hund’s coupling is also large in materials with partly occupied $3d$ or $5f$ shells. Material with partly occupied $3d$ shells.

The high density of states at the Fermi level is difficult to achieve; usually, $2p$ bandwidths are large, meaning the Stoner criterion is unlikely to be satisfied. However, in perovskite oxides, the highest occupied molecular orbital oxygen $t_{2g}$ band is very flat and does not hybridize with any other orbitals [8]. This makes it an excellent candidate for realizing Stoner ferromagnetism, if sufficient hole density is achieved.

Simple charge counting dictates that combining one perovskite with neutral (100) layers and another with charged (100) layers results in an interface with additional electrons or holes (termed the $n$-type or $p$-type interface, respectively), to maintain charge neutrality of the complete structure [9]. Such charge-imbalanced interfaces between two perovskites have been widely studied, because an interface with a two-dimensional electron gas based on $d$ orbitals exhibits properties such as metallicity [10], magnetism [11], and superconductivity [12].

In this Letter, we show the $p$-type interface of $d^0$ perovskites [14,16,17] to be ferromagnetic and half-metallic. As the sample system, we study SrTiO$_3$/KTaO$_3$ superlattices with two similar ($p$ or $n$) interfaces, starting with 1.5 unit cells of both perovskites. This results in a structure with one hole or one electron per supercell compared to nominalionic charges (Fig. 1). We compare the results of $ab$ initio LSDA + $U$, GGA + $U$, and HSEsol hybrid functional [18] methods, using the VASP [19] code and projector augmented wave [20] potentials. The generalized gradient approximation (GGA) employed is PBEsol [21]. The in-plane lattice constant is fixed to the calculated SrTiO$_3$ lattice constant, to model epitaxy on a SrTiO$_3$ substrate. Ionic relaxations are performed to allow for ionic compensation of the interface dipoles, although their effect is expected to be very small [17].
Considering two-body Coulomb repulsion $U$ or nonlocal exchange (by HSEsol) is necessary due to the failure of local spin density approximation (LSDA) or GGA to properly predict the behavior of partly occupied oxygen $p$ or Ti $d$ orbitals. Magnetic properties are very sensitive to electron localization and small changes in partial occupancies, and $d^0$ magnetism is poorly described in local exchange-correlation approximations [22]. For DFT + $U$, we use the Dudarev et al. [23] implementation. We vary the $U_{\text{eff}} = U - J$ parameter, the difference between local Coulomb repulsion $U$ and exchange interaction $J$, between 0 and 8 eV to study the effect of correlations. Magnetic metals yield the best agreement with experiment at $U$ values smaller than those calculated from first principles [24], as the fully localized limit double counting correction exaggerates magnetic moments and band gaps. Therefore, we expect $U_{\text{eff}}$ of 2–5 eV (on $p$ orbitals) and 3–7 eV (on $d$ orbitals) to yield correct behavior, based on earlier experimental [25,26] and computational [7,14,23,26,27] studies considering $U$ and $J$. Further insight into suitable $U_{\text{eff}}$ is obtained by comparing the magnetization energies with HSEsol calculations, as in Ref. [28].

The SrTiO$_3$/KTaO$_3$ superlattices with two $p$ (hole-doped) interfaces are metallic up to $U_{\text{eff}} = 6$ eV as well as in HSEsol. The extra holes are confined in the SrTiO$_3$ layers only. The total $p$ (hole-doped) superlattice magnetization and energy difference between FM, antiferromagnetic (AFM), and paramagnetic (PM) states, as a function of $U_{\text{eff}}$, are shown in Fig. 2(a). The DFT + $U$ calculations were done in a $p(2 \times 2)$ supercell to find possible antiferromagnetic orderings. The GGA/LSDA system has a partially spin-polarized FM ground state. A small on-site Coulomb interaction considerably increases the energy difference in favor of magnetic ordering and results in complete spin polarization of the conduction holes with realistic $U_{\text{eff}}$ values (2–5 eV). With the HSEsol hybrid functional, as well, half-metallicity is obtained. The HSEsol FM phase energy is indicated in Fig. 2(a). This would support choosing $U_{\text{eff}} = 4$ eV for our system in the spirit of Hong et al. [28].

A charge ordered, symmetry broken AFM solution has 2D AFM ordering of chains of parallel spins. It displays a Mott transition to an insulating state for $U_{\text{eff}} = 6$ eV and higher, but it is the ground state only at unphysical $U_{\text{eff}} \approx 7$ eV.

With the $n$ (electron-doped) superlattice, on the other hand, the ground state is paramagnetic metal for small $U_{\text{eff}}$. The electrons are confined in the SrTiO$_3$ layers only. At large $U_{\text{eff}}$ and with the HSEsol hybrid functional, a partially spin-polarized FM state is found, but an AFM phase is energetically preferred [Fig. 2(b)] for almost all $U_{\text{eff}}$. The HSEsol energy difference between the FM and PM phases is only 10 meV per $p(2 \times 2)$ supercell. This would suggest selecting $4 \text{ eV} < U_{\text{eff}} < 5 \text{ eV}$ for $d$ orbitals; however, as seen in Fig. 2(b), the ground state is highly sensitive to $U_{\text{eff}}$. The energy differences are large only with high $U_{\text{eff}}$, and half-metallicity or Mott insulation are not present. This is in accordance with paramagnetism observed below $d^1$ doping of Ti $d$ orbitals in the bulk [29]. Complex octahedral rotations [16] and charge and spin ordered phases on the $d$ orbitals [30] depending on superlattice geometry, strain, and $U_{\text{eff}}$ might be present but are not studied here, because the rotations are not present at room temperature in the constituent perovskites.

Clearly, in the $d^0$ superlattice case, interface holes magnetize much more readily than electrons. To consider the effect of 2D localization on the magnetization of the hole gas, we study a thicker superlattice, where the magnetized hole or electron might spread over 5.5 unit cells of...
SrTiO₃. The magnitude of magnetization is the same regardless of the thickness of the SrTiO₃ layer, demonstrating that ferromagnetism is a true interface effect. The hole density is strongly localized at the interface; in the middle of the 5.5 unit cell SrTiO₃ layer, i.e., only two unit cells away from the interface, maximum magnetization density is 20% of that at the interface. The strong 2D confinement is comparable to electron gas in n-type interfaces [31]. Coupling of the magnetizations at the two interfaces is negligible, showing that a single interface has a stable FM ground state.

The presence of vacancies can be another source of possible magnetic signals in experiments. Ferromagnetic behavior in oxide materials is often attributed to oxygen vacancies forming localized magnetic moments, as electrons are donated to the surrounding cation d orbitals. In the n-type interface, the lack of simple FM coupling in the electron-doped SrTiO₃ layer indicates that oxygen vacancies, contributing electrons to the d band, would not cause ferromagnetism. In the p-type case, they would counteract hole doping and prevent magnetization. To study the effect vacancies have at interfaces, we calculate a 1.5/1.5 superlattice \( p(2 \times 2) \) supercell with an electron (or hole) donating O (or K) vacancy. At intermediate \( U_{\text{eff}} \) values, n-type superlattices with O or K vacancies have close to zero magnetic moment, while p superlattices with O or K vacancies form completely spin-polarized metallic states. The calculated p superlattice magnetic moment is equal to the amount of holes contributed by the interface and the vacancy combined. This means that the interface region is dominated by intrinsic doping, and vacancies will change only the total magnitude of the moment. Metallicity is similarly obtained for 25% oxygen vacancy concentration in SrTiO₃/LaAlO₃ interfaces [15], indicating that a higher vacancy concentration is needed to change the interface to insulating.

Finally, to find out the effect of the perovskite A and B ions on the localization and magnetization of the hole, we study similar 1.5/1.5 n- and p-type SrTiO₃/KNbO₃, BaTiO₃/KNbO₃, CaTiO₃/KNbO₃, SrTiO₃/NaTaO₃, BaTiO₃/NaTaO₃, and CaTiO₃/NaTaO₃ superlattices, all of which have one nonpolar and one polar \( d^0 \) perovskite. The obtained behavior of holes and electrons in all structures is identical to the model SrTiO₃/KTaO₃ system, which demonstrates that ferromagnetism is a general feature of \( p \)-type interfaces of \( d^0 \) perovskites. Complete spin polarization of the holes is obtained with small values of \( U_{\text{eff}} \), with energies similar to the SrTiO₃/KTaO₃ case.

To study predicted magnetization, ultrathin epitaxial films of \( d^0 \) perovskite KTaO₃, KNbO₃, and NaNbO₃ were grown onto Ti-terminated SrTiO₃ (001) single-crystal substrates by in situ pulsed laser deposition using a KrF excimer laser and high oxygen pressure (30 Pa during deposition and 10⁵ Pa during postdeposition cooling). The microstructure of the KTaO₃/SrTiO₃ interface was characterized by aberration-corrected scanning transmission electron microscopy employing the high-angle annular dark field (HAADF) technique. Crossover sections for scanning transmission electron microscopy analysis were prepared by standard mechanical thinning, precision polishing, and Ar ion milling.

Figure 3(a) displays an HAADF image with the viewing direction along the crystallographic [100] direction of the SrTiO₃ substrate. From local fast Fourier transform analysis [inset in Fig. 3(a)], full epitaxial growth of KTaO₃ on SrTiO₃ with a KTaO₃[100] [001] \( \parallel \) SrTiO₃[100][001] relationship is derived. The growth is coherent with the in-plane lattice parameter of the KTaO₃ film matching that of the SrTiO₃ substrate. No dislocations are observed to relax the lattice strain (−2.1%) within the first 10 nm of the KTaO₃ film. In high-resolution HAADF imaging or so-called Z-contrast imaging, the atoms appear with bright contrast on a dark background. An intensity profile across the interface (from A to B) is shown in Fig. 3(b). In the KTaO₃ film, strong peaks from the Ta atoms are easily determined, whereas low intensity peaks from K atoms are not resolved. At the interface, two adjacent low intensity peaks due to Ti and K atoms are visible, indicating the formation of a \( p \)-type interface. Because the difference in intensity between the Ti and K peaks is below noise level, it is impossible to unambiguously identify the interface structure. While TiO₂ termination of the SrTiO₃ substrate and the formation of a KO atomic layer at the heterointerface are most likely, some degree of intermixing and off-stoichiometry cannot be excluded.

![Figure 3](image-url)
Optical constants in the KTaO₃/SrTiO₃ heterostructures were determined by using variable angle spectroscopic ellipsometry and the WVASE32 software package for data analysis [32]. The model analysis considering a stack of substrate, film, surface roughness, and ambient air failed, while a nearly perfect fit was obtained when an additional nanolayer was introduced below the film [Fig. 4(a)]. The thickness of the KTaO₃ film determined from the ellipsometric data is equal to that determined by x-ray reflectivity, evidencing correctness of the fitting procedure. The thickness of the interfacial layer is about 2 nm. The spectral features of the interfacial nanolayer resemble those of the SrTiO₃ substrate at large photon energies E > 3 eV, indicating that the origin of the interfacial layer is related to changes in electronic states in SrTiO₃. A profound absorption tail at E < 3 eV suggests the presence of in-gap states in the interfacial SrTiO₃ nanolayer.

Magnetic measurements were performed in the film plane by a Quantum Design SQUID magnetometer (MPMS XL 7 T). Reciprocating sample transport enabled high sensitivity (10⁻⁸ emu). The diamagnetic response of the reference SrTiO₃ substrate was separately measured and used to extract the magnetization of the film and interface from the response of the film-substrate stack. Additionally, annealing of the samples in an oxygen atmosphere (450–500 °C, 20–24 hours) was performed in order to check the possible influence of oxygen vacancies. Ferromagnetic-type behavior is observed in all samples [Fig. 4(b)], both as-deposited and after annealing. The saturation moments [33] do not decrease after annealing and they remain practically unchanged with decreasing temperature from 300 to 20 K, which indicates ordering temperatures well above room temperature.

As stated, in d⁰ bulk perovskites and superlattices, the d band is very wide, and the oxygen 2p band has a higher density of states (DOS) and the exchange interaction J is higher for oxygen p than transition metal d states [7]. The HSEsol hybrid functional yields a half-metallic density of states where the 2p band edges of the two spins are separated by over 1 eV in the p interface case [Fig. 5(a)]. For the n-type interface FM phase (not pictured), on the other hand, the HSEsol Ti d band edge stays almost the same for both spins, although exchange splitting of the peak occurs. The strength of magnetic effects in these interfaces is illustrated by the HSEsol magnetization energy, which is 340 meV for p-type interface but only 10 meV for n-type interface per p(2 × 2) supercell.

In the Stoner ferromagnetic transition, the spike in the DOS crosses the Fermi level when spin polarization takes place. This also happens in the LSDA and GGA DOS [Fig. 5(b)], and the system seems to be close to a fully half-metallic state. A half-metallic FM ground state requires a small local Coulomb repulsion [Fig. 5(c)] or inclusion of nonlocal exchange [Fig. 5(a)] on the oxygen p orbitals. The electron-doped superlattice with small Ueff, on the other hand, retains a paramagnetic DOS virtually identical to the GGA DOS, and nonlocal exchange causes only partial magnetization. The hole-doped system clearly satisfies the Stoner criterion JD(EF) > 1, while the electron-doped does not. The same mechanism has been suggested for hole-doped ZnO [7], where nonintrinsic doping methods have been considered.

In summary, we report experimental evidence and ab initio analysis of d⁰ ferromagnetism at charge-imbalanced perovskite interfaces. We suggest that ferromagnetic ordering and half-metallicity is present in hole-doped d⁰ perovskites due to large p orbital exchange splitting and the high density of states at the top of the oxygen p band under sufficient doping. The reason for the general scarcity of d⁰ ferromagnets is the difficulty of doping the p valence band. High hole concentrations, however, are easily obtained with intrinsic doping by interfaces. Even a single interface has sufficient DOS for ferromagnetism, since the carriers are strongly 2D localized at the interface region. Electron-doped d⁰ perovskites are ordinary metals, as the bottom of the cation d band has larger dispersion, but they are susceptible to partial magnetization and possible complex magnetic ordering patterns under 2D localization.

![FIG. 4 (color online).](Image)

(a) Absorption coefficient α as a function of photon energy E in the SrTiO₃ substrate (blue curve), KTaO₃ film (black curve), and interfacial nanolayer (red curve). The spectra are obtained from ellipsometric data for the model stack shown schematically. (b) SQUID measured total magnetization as a function of external magnetic field determined at room temperature in as-deposited 10 × 5 mm² films of KTaO₃/SrTiO₃ (red curve), KnBO₃/SrTiO₃ (blue curve), and NaNbO₃/SrTiO₃ (black curve).

![FIG. 5.](Image)

Densities of states for 1.5/1.5 SrTiO₃/KTaO₃ p-type superlattice with (a) HSEsol hybrid functional, (b) GGA, and (c) GGA + U, Ueff = 2 eV.
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