

Fabrication of half metallicity in a ferromagnetic metal

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We investigate the growth of half metallic phase in a ferromagnetic material using *state-of-the-art* full potential linearized augmented plane wave method. To address the issue, we have substituted Ti at the Ru-sites in SrRuO_3 , where SrRuO_3 is a ferromagnetic material. Calculated results establish Ti^{4+} valence states (similar to SrTiO_3), which was predicted experimentally. Thus, Ti substitution dilutes the Ru-O-Ru connectivity, which is manifested in the calculated results in the form of significant band narrowing leading to finite gap between t_{2g} and e_g bands. At 75% substitution, a large gap ($> 2\text{eV}$) appears at the Fermi level, ϵ_F in the up spin density of states, while the down spin states contributes at ϵ_F characterizing the system a half-metallic ferromagnet. The $t_{2g} - e_g$ gap can be tailored judiciously by tuning Ti concentrations to minimize thermal effects, which is often the major bottleneck to achieve high spin polarization at elevated temperatures in other materials. This study, thus, provides a novel but simple way to fabricate half-metallicity in ferromagnetic materials, which are potential candidates for spin-based technology.

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The search of half metallic ferromagnetic materials has seen an explosive growth in the recent times due to its potential technological applications. In these materials, the electronic density of states (DOS) at the Fermi level, ϵ_F corresponds to only one kind of spin, while the other spin density of states exhibit an energy gap at ϵ_F . Thus, in the polarized condition, electronic conduction strongly depends on the spin of the charge carriers; the material is insulating for one kind of spin and metallic for the other. This unique property makes them ideal candidates for the development of spin-based electronics. Various theoretical studies predicted half metallicity in Heusler alloys [1], double perovskites [2], manganates [3], CrO_2 [4], graphene nanoribbons [5] etc. However, experimental studies on very few materials such as manganates [3] and CrO_2 [4], etc. exhibit half metallicity at low temperatures. Thermal fluctuations often lead to a reduction in spin polarization at elevated temperatures [6] making it difficult for technological applications.

In this study, we investigate the evolution of the electronic density of states in $\text{SrRu}_{1-x}\text{Ti}_x\text{O}_3$ as a function of x . SrRuO_3 is a ferromagnetic metal with Curie temperature of 165 K. Spin polarization at ϵ_F is found to be negative in the ferromagnetic ground state [7, 8]. SrTiO_3 , on the other hand, is a band insulator. Various experimental studies [9, 10] suggest $(4+)$ valence state of Ti in the intermediate compositions (similar to SrTiO_3), which corresponds to $3d^0$ electronic configuration. Thus, in addition to disorder effect, Ti substitution leads to a dilution of Ru-O-Ru connectivity. Transport measurements in $\text{SrRu}_{1-x}\text{Ti}_x\text{O}_3$ exhibit a range of novel phase transitions involving disorder induced correlated metal, Anderson insulator, correlated insulator and band insulators [11] for different values of x .

Using *ab initio* calculations, we find that Ti substitution at Ru-sites in ferromagnetic SrRuO_3 leads to half

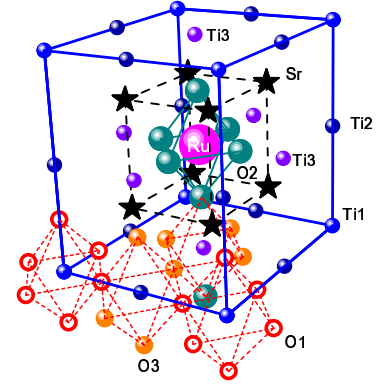


FIG. 1: (color online) Crystal structure of $\text{SrRu}_{0.25}\text{Ti}_{0.75}\text{O}_3$. In order to obtain the structure of SrRuTiO_3 , we replaced Ti_2 by Ru, and all the Ti and Ru sites are made equivalent.

metallicity. Here, reduced Ru-O-Ru connectivity due to Ti-substitution leads to significant narrowing of Ru $4d$ band and thus, the up spin band moves below ϵ_F . Interestingly, the energy gap between t_{2g} and e_g bands can be tuned by Ti-concentration. 75% substituted sample exhibits gap as high as 2 eV. Experimental realization of such method on different systems would provide a new direction in the search of HMFs for spin-based technology.

The electronic density of states of $\text{SrRu}_{1-x}\text{Ti}_x\text{O}_3$ for $x = 0.0, 0.5, 0.75$ and 1.0 were calculated using state-of-the-art full potential linearized augmented plane wave method (FLAPW) within the local spin density approximations (LSDA) using WIEN2K software [12]. The crystal structure of SrTiO_3 is cubic with the lattice constant, $a = 3.905 \text{ \AA}$. SrRuO_3 possesses close to cubic structure with small orthorhombic distortion. This is manifested clearly by the similar density of states (DOS) of SrRuO_3 in real structure vis-a-vis in the equivalent cubic structure [7]. Ti-substitution in SrRuO_3 leads the system towards cu-

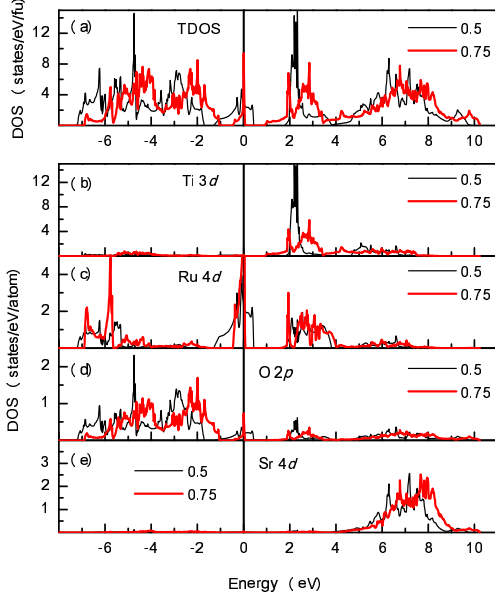


FIG. 2: (color online) (a) TDOS, (b) Ti 3d PDOS, (c) Ru 4d PDOS, (d) O 2p PDOS and (e) Sr 4d PDOS of $\text{SrRu}_{1-x}\text{Ti}_x\text{O}_3$. Thin and thick solid lines represent DOS corresponding to $x = 0.5$ and 0.75 , respectively.

bic structure. Thus, we have considered cubic structure for all the calculations in this study. A typical unit cell for $\text{SrRu}_{0.25}\text{Ti}_{0.75}\text{O}_3$ is shown in Fig. 1. There are 8 formula units in the unit cell constructed by doubling the lattice constant of SrTiO_3 . In order to preserve cubic symmetry, three types of Ti are considered occupying corners (Ti1), edge centers (Ti2) and face centered positions (Ti3). The body centered position is occupied by Ru. There are three non-equivalent oxygens; O1 forms the octahedra around Ti1-sites, O2 forms the octahedra around Ru-sites and the rest of the oxygen positions are occupied by O3. Thus, the connectivity between Ru-sites occurs via Ru-O2 bondings. The muffin-tin radii (R_{MT}) for Sr, Ru, Ti and O were set to 1.16 Å 0.95 Å 0.95 Å and 0.74 Å respectively. The convergence for different calculations were achieved considering 512 k points within the first Brillouin zone. The error bar for the energy convergence was set to < 0.25 meV per formula unit. In every case, the charge convergence was achieved to be less than 10^{-3} electronic charge.

In Fig. 2, We show the total DOS calculated for $\text{SrRu}_{1-x}\text{Ti}_x\text{O}_3$ ($x = 0.5$ and 0.75) and the partial DOS obtained by projecting the eigenstates onto the Ti 3d, Ru 4d, O 2p and Sr 4d states. The figure exhibits 5 distinctly separable features. The energy region -1.5 eV to -5 eV is primarily contributed by O 2p partial DOS with negligible contributions from other electronic states. Thus, these contributions are characterized due to the non-bonding O 2p states. Sr 4d partial DOS shown in Fig. 2(e) appear above 5 eV. The peak appears to shift towards higher energy with increasing x . This can be

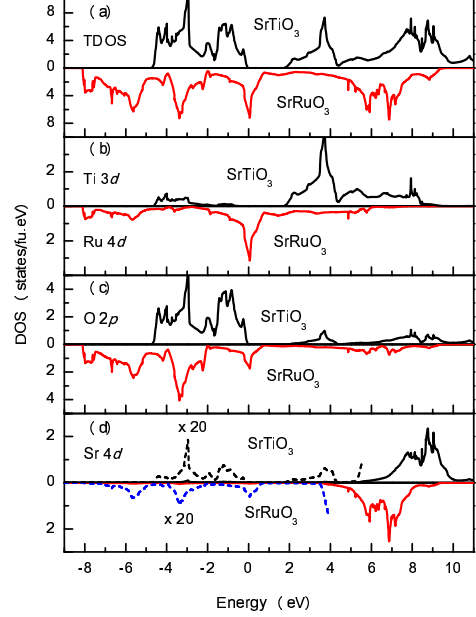


FIG. 3: (color online) (a) TDOS, (b) Ti 3d and Ru 4d PDOS, (c) O 2p PDOS and (d) Sr 4d PDOS of SrTiO_3 and SrRuO_3 . Dashed line represent Sr 4d PDOS rescaled by 20 times.

understood by comparing the same in the end members, SrTiO_3 and SrRuO_3 as demonstrated in Fig. 3. Sr 4d states appear at much higher energies in SrTiO_3 compared to that in SrRuO_3 . One reason for such a large shift may be related to the shift of the Fermi level to the top of the O 2p band in SrTiO_3 . However, the shift of Sr 4d band in the intermediate compositions, where the Fermi level is pinned by the occupancy of the Ru 4d band, indicates that the Madelung potential at Sr-sites increases with the increase in Ti concentrations.

Ti 3d partial DOS appears 2 eV above the Fermi level. This clearly demonstrates that the occupancy of Ti 3d states is essentially zero and hence correspond to Ti^{4+} valency. Such valence states was predicted in the x-ray photoemission spectra [9]. This study provides evidence of such effect theoretically within the effective single particle approach itself. The width of the Ti 3d t_{2g} band is significantly small in $x = 0.5$ sample (~ 0.65 eV), which increases to 1.5 eV in $x = 0.75$ sample and 2.5 eV at $x = 1.0$ (see Fig. 3).

Ru 4d partial DOS exhibit three regions. The narrow and intense feature between the energy range -1.6 to 0.5 eV correspond to the electronic states having t_{2g} symmetry. The electronic states above 1.8 eV appears due to Ru 4d states having e_g symmetry. Notably, the O 2p states also contribute in all the three energy regions. Thus, DOS appearing below -5 eV can be attributed to the Ru 4d - O 2p bonding states having a large O 2p character, and the energy region above -1.5 eV are the anti-bonding states having primarily Ru 4d character. Most interestingly, both the compounds exhibit metallic

ground state. However, the t_{2g} bandwidth, W reduces significantly with the increase in x . While W is close to 2.6 eV in SrRuO_3 , it is about 1.7 eV for $x = 0.5$ and 0.54 eV for $x = 0.75$. Such reduction in W is understandable as Ti-substitution leads to a significant reduction in the hopping interaction strength due to the reduced degree of Ru-O-Ru connectivity. This is clearly evident in Fig. 1; if we assume homogeneous distribution of Ru and Ti atoms in the solid, all the RuO_6 octahedra are separated by TiO_6 octahedra at $x = 0.5$. At $x = 0.75$, the number of Ru-[O-Ti]-Ru connectivity reduces to half of that at $x = 0.5$. Subsequently, U/W (U = local Coulomb interactions strength) will increase significantly and presumably play a role in the transport properties in these compositions [11].

In order to understand the bonding of Ru 4d electronic states with various O 2p states, we compare the Ru 4d t_{2g} and e_g bands with the 2p bands corresponding to O1, O2 and O3 for $x = 0.75$ and 0.5 sample in Fig. 4(a) and 4(b), respectively. All the oxygens are equivalent in the $x = 0.5$ sample. The energy distribution of O2 2p partial DOS is almost identical in Fig. 4(a) to that observed in Ru 4d partial DOS. This is expected as the RuO_6 octahedra is formed by O2 atoms only. The width of the O2 2p band is significantly larger than that of O1 and O3. The most interesting observation is that the t_{2g} and e_g bands are separated by a distinct energy gap. This gap is already visible in Ru 4d partial DOS of $x = 0.5$ sample in Fig. 4(b) and is absent in SrRuO_3 as shown in Fig. 3 and in the literature as well [7, 13].

We calculate the crystal field splitting of the Ru 4d band by measuring the separation of the center of gravity of the Ru 4d t_{2g} and e_g bands as shown in Fig. 4 by closed circles in both the compositions. It is evident that crystal field splitting, Δ remains almost the same (~ 2.1 eV) in both the compositions and is very close to 2 eV found in SrRuO_3 . Thus, the large energy gap between the t_{2g} and e_g bands appears purely due to the band narrowing. Such effect has strong implication in the magnetic phase as described below.

It is already well established that the magnetic ground state can be exactly described by these band structure calculations [7, 14, 15, 16]. Thus, we have calculated the ground state energies for ferromagnetic arrangement of moments of the constituents using local spin-density approximations. Interestingly, the eigen energy for the ferromagnetic ground state in $x = 0.5$ sample is 5.67 meV/fu lower than the lowest eigen energy for the non-magnetic solution. This is higher than 1.2 meV/fu observed in SrRuO_3 in real structure and significantly smaller than 30.4 meV/fu observed in the equivalent cubic structure of SrRuO_3 . This energy difference between the non-magnetic and magnetic solutions increases to 33.95 meV/fu in $x = 0.75$. All these results suggest that the stability of the ferromagnetic ground state increases with the decrease in the degree of charge delocalization of the

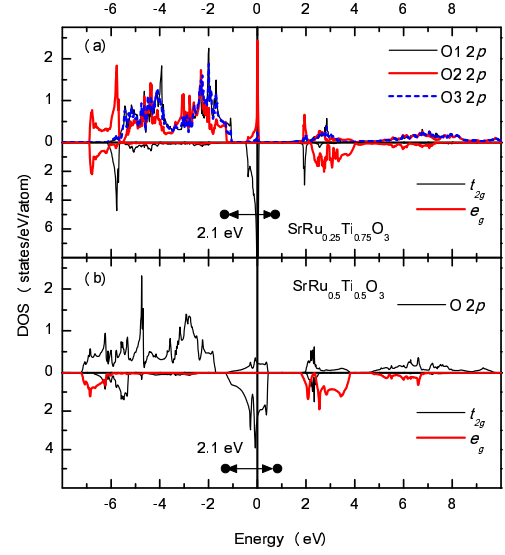


FIG. 4: (color online) Ru 4d partial DOS with t_{2g} and e_g symmetry are compared with the O 2p partial DOS in (a) $\text{SrRu}_{0.25}\text{Ti}_{0.75}\text{O}_3$ and (b) $\text{SrRu}_{0.5}\text{Ti}_{0.5}\text{O}_3$.

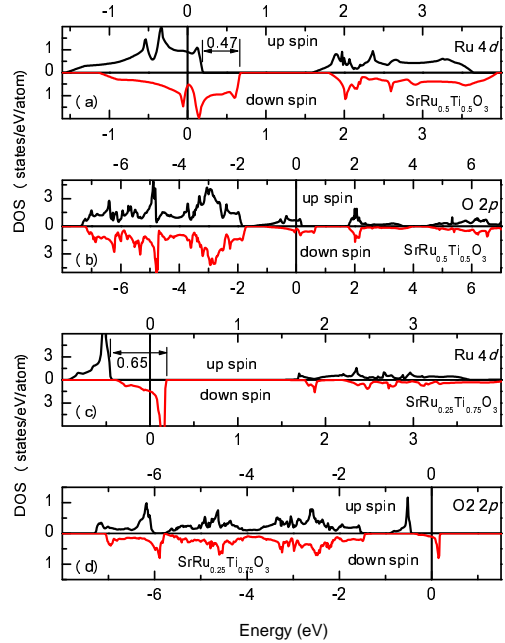


FIG. 5: (color online) Up and down spin density of states corresponding to (a) Ru 4d in $\text{SrRu}_{0.5}\text{Ti}_{0.5}\text{O}_3$, (b) O 2p in $\text{SrRu}_{0.5}\text{Ti}_{0.5}\text{O}_3$, (c) Ru 4d in $\text{SrRu}_{0.25}\text{Ti}_{0.75}\text{O}_3$, and (d) O 2p in $\text{SrRu}_{0.25}\text{Ti}_{0.75}\text{O}_3$. This figure demonstrates that band narrowing in Ru 4d band leads to a gap in the up spin channel leading to half metallicity.

valence electrons.

The spin magnetic moment centered at Ru-sites is found to be about $0.6 \mu_B$ in $x = 0.5$ sample. Interestingly, magnetic moment at the interstitial electronic states is significantly large ($\sim 0.36 \mu_B$). The moment at the O sites is about $0.05 \mu_B$. The Ti sites also ex-

hibit very small moment ($\sim -0.03 \mu_B$). Thus the total magnetic moment of the solid becomes $1.24 \mu_B$ per Ru-atom. This is very similar to that observed ($1.2 \mu_B$) in SrRuO_3 . The magnetic moments increase significantly with the increase in x . The moments at Ru site becomes $0.88 \mu_B$ in $x = 0.75$ sample. The moments of the interstitial states and $2p$ states at O2 sites also enhance to $0.66 \mu_B$ and $0.066 \mu_B$, respectively. Thus, the total moment turns out to be $1.99 \mu_B$, which is very close to the spin only value of $2 \mu_B$ corresponding to Ru $4t_{2g}^4$ electronic configuration. It is to note here that although the local moment of the highly extended $4d$ states is significantly smaller than the spin only value as opposed to the case in $3d$ transition metal oxides [15], Ru $4d$ moment induces a large degree of polarization in the interstitial and O $2p$ electrons. These results evidently suggest applicability of Stoner description to capture magnetic properties of these systems.

In order to investigate the exchange splitting and the character of density of states in the vicinity of ϵ_F , we plot the spin-resolved DOS corresponding to Ru $4d$ and O $2p$ partial DOS in Fig. 5. In the $x = 0.5$ sample, both the up and down spin states contribute at ϵ_F and the exchange splitting is found to be about 0.47 eV. This is again very similar to the case in SrRuO_3 [7]. The exchange splitting increases to 0.65 eV in $x = 0.75$ sample as shown in the figure. Interestingly, the up spin band moves significantly below ϵ_F and the contributions at ϵ_F appears only due to the down spin states indicating a half-metallic behavior. No contribution of the up spin states observed in the total density of states (not shown here). Considering the paucity of half-metallic materials for various technological applications, achieving half metallicity in the ferromagnetic SrRuO_3 by Ti-substitution is remarkable.

It is believed that the half metallicity can be achieved via strong $d-d$ hybridization in Heusler alloys involving two transition metal elements in the compound [17]. In transition metal oxides, often doping of large amount of electrons or holes leads to a shift of the Fermi level towards the energy gap of one spin channel leading to half metallicity [3]. The primary difficulty to use these systems in technological applications is the loss of half metallicity at elevated temperatures, where thermal excitations leads to significant mixing of various spin channels due to small energy gap at ϵ_F [6]. In the present case, mechanism to achieve half metallicity is simple and easily achievable experimentally. The most important aspect is that the energy gap between t_{2g} and e_g bands can be tailored judiciously by tuning the composition to minimize thermal effects.

In summary, we investigate the possibility of fabricating half metallicity by Ti-substitution at the Ru-sites in a ferromagnetic material, SrRuO_3 . The calculated results using FLAPW method within the local spin density approximations reveal tetravalency of Ti in all the compositions consistent with the experimental predictions.

The Ru $4d$ band exhibit significant narrowing with the increase in Ti-substitution; the crystal field splitting remains almost the same across the whole series. Thus, an energy gap develops between the t_{2g} and e_g bands, which gradually grows with the increase in x . Consequently, the up spin density of states exhibit an energy gap at the Fermi level, while the down spin states still contribute leading to half metallicity. Most interestingly, the $t_{2g} - e_g$ gap can be engineered by tuning x and thus spin mixing effects due to thermal excitations can be minimized. This study thus provide a novel but simple way to fabricate half metallicity in ferromagnetic materials, which are potential candidates for spin based technology. Experimental realization of this method would help both chemists and physicists to cultivate new materials. In addition, this study demonstrates that effective single particle approaches provide a remarkable description of the electronic properties of these systems, which are predicted experimentally.

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