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 ($>2$eV) appears at the Fermi level, $\epsilon_F$ in the up spin density of states, while the down spin states contributes at $\epsilon_F$ 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, $\epsilon_F$ corresponds to only one kind of spin, while the other spin density of states exhibit an energy gap at $\epsilon_F$. 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 SrRu$_{1-x}$Ti$_x$O$_3$ as a function of x. SrRuO$_3$ is a ferromagnetic metal with Curie temperature of 165 K. Spin polarization at $\epsilon_F$ 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 [3,10] suggest (4+) valence state of Ti in the intermediate compositions (similar to SrTiO$_3$), which corresponds to 3$d^0$ electronic configuration. Thus, in addition to disorder effect, Ti substitution leads to a dilution of Ru-O-Ru connectivity. Transport measurements in SrRu$_{1-x}$Ti$_x$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 metallicity. Here, reduced Ru-O-Ru connectivity due to Ti-substitution leads to significant narrowing of Ru 4$d$ band and thus, the up spin band moves below $\epsilon_F$. 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 SrRu$_{1-x}$Ti$_x$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 Å. 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 [2]. Ti-substitution in SrRuO$_3$ leads the system towards cu-
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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-O]-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 4$d$ electronic states with various O 2$p$ states, we compare the Ru 4$d$ $t_{2g}$ and $e_g$ bands with the 2$p$ 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 2$p$ partial DOS is almost identical in Fig. 4(a) to that observed in Ru 4$d$ partial DOS. This is expected as the RuO$_6$ octahedra is formed by O2 atoms only. The width of the O2 2$p$ 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 4$d$ 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 [1,2].

We calculate the crystal field splitting of the Ru 4$d$ band by measuring the separation of the center of gravity of the Ru 4$d$ $t_{2g}$ and $e_g$ bands as shown in Fig. 4 by closed circles in both the compositions. It is evident that crystal field splitting, $\Delta$ remains almost the same ($\sim 2.1$ 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 [1,4,10]. 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 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 O$_2$ 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 4$d^5$ electronic configuration. It is to note here that although the local moment of the highly extended 4$d$ states is significantly smaller than the spin only value as opposed to the case in 3$d$ transition metal oxides [8], Ru 4$d$ moment induces a large degree of polarization in the interstitial and O 2$p$ 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 $\epsilon_F$, we plot the spin-resolved DOS corresponding to Ru 4$d$ and O 2$p$ partial DOS in Fig. 5. In the $x = 0.5$ sample, both the up and down spin states contribute at $\epsilon_F$ and the exchange splitting is found to be about 0.47 eV. This is again very similar to the case in SrRuO$_3$ [6]. 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 $\epsilon_F$ and the contributions at $\epsilon_F$ 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 [12]. 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 $\epsilon_F$ [3]. 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 4$d$ 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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