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The search for new spintronic materials: half-metallic antiferromagnets and diluted magnetic semiconductors

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Abstract

Based on the electronic structure studies, we propose that the double perovskite $LaVO_3/ARuO_3$ superlattice (A = Ca, Sr and Ba) and thiospinel $Mn(CrV)S_4$ and $Fe_{0.5}Cu_{0.5}(V_{0.5}Ti_{1.5})S_4$ are potential candidates for half-metallic antiferromagnets (HM-AFMs). We have also explored the effect of the Li intercalation on the electronic and magnetic properties of transition-metal (TM) doped anatase TiO_2. We propose a potential spintronic and electrochromic device made of Li intercalated Mn-doped TiO_2, which is controlled by the electric field. For (Fe, Cu) co-doped ZnO, the charge transfer between Fe and Cu leads to ferromagnetism via a type of the double-exchange mechanism.

1. Introduction

Spintronics, namely spin-based electronics, is a new generation of microelectronics which utilizes both charge and spin degrees of freedom of carriers. Half-metals and diluted magnetic semiconductors (DMSs) are expected to be promising materials for spin-based multifunctional devices [1]. In half-metals, the conduction electrons at the Fermi energy E_F are 100% spin polarized. Since the first theoretical report of the Heusler half-metallic (HM) ferromagnet NiMnSb by de Groot *et al* [2], much effort has been made to develop HM magnetic materials. Typical examples are rutile CrO_2 [3], mixed-valence perovskite $La_{0.7}Sr_{0.3}MnO_3$ [4], double perovskite Sr_2FeMoO_6 [5], spinel $FeCr_2S_4$ [6], Mn-doped GaAs [7, 8], etc. The HM property is considered to be related closely to the colossal magnetoresistance (CMR) phenomena observed in perovskites [4, 9] and double perovskites [5]. In particular, the HM antiferromagnet (HM-AFM) attracts great attention because it is a non-magnetic metal but its conduction electrons

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are perfectly spin-polarized. It can be used as a probe of the spin-polarized scanning tunnelling microscope without perturbing the spin-character of samples. Further, the HM-AFM will play a vital role in future spintronic devices that utilize the spin polarization of the carriers.

DMSs are promising spintronic materials due to their easy integration into existing semiconductor devices. An ideal DMS must satisfy certain conditions, such as a high Curie temperature (T_C) and the easy incorporation of p- and n-type dopants. The ferromagnetic (FM) behaviour with $T_C \sim 110$ K of Mn-doped GaAs has attracted great attention [10], and it has been suggested that delocalized holes mediate the FM interaction between Mn spins [11]. The recent effort has been focused on developing a new FM-DMS operating above room temperature.

In this work, we have studied and designed new spintronic materials and devices. The main materials investigated in this study are the HM-AFMs and oxide-based transparent DMSs. In section 2, we have theoretically designed new HM-AFMs, based on double perovskite (section 2.1) and thiospinel (section 2.2) systems. In section 3, we have explored the electronic structures and the magnetic properties of transition-metal (TM) doped TiO_2 with intercalating Li (section 3.1) and (Fe, Cu) co-doped ZnO (section 3.2). A new potential spintronic and electrochromic device is proposed by employing the Li-intercalation method.

As a band method, we have used the linearized muffin-tin orbital (LMTO) method in the local spin-density approximation (LSDA). To explore the effects of the Coulomb interaction U and the spin–orbit (SO) interaction, we have also employed the LSDA + U + SO method by incorporating U and the SO interaction [12].

2. Half-metallic antiferromagnets: HM-AFMs

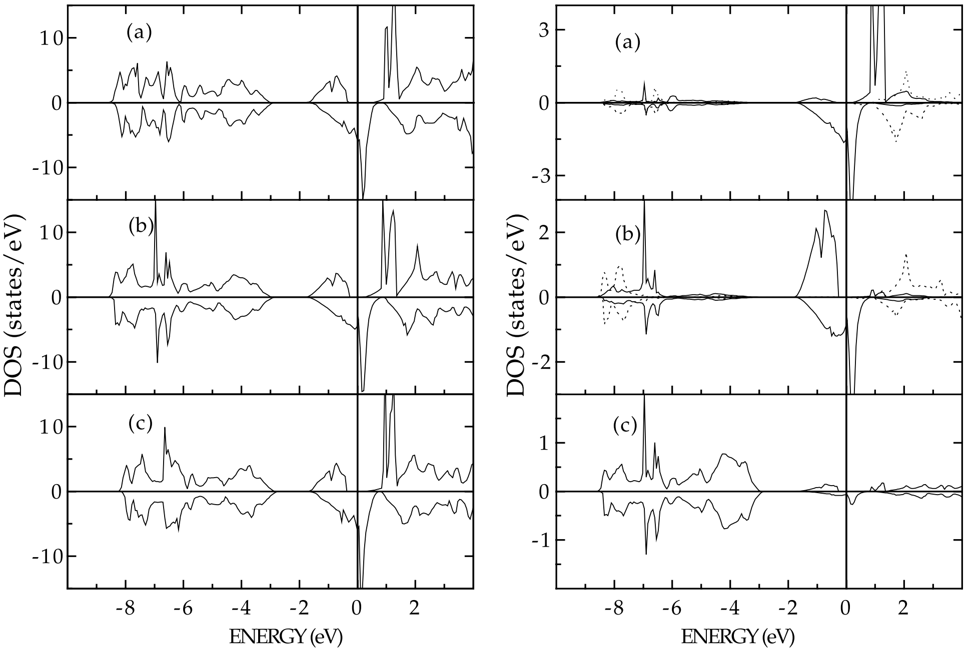
The first proposed HM-AFM is $V_7MnFe_8Sb_7In$, which is a derivative of the Heusler compound [13]. Another possibility was suggested by Pickett [14] in the double perovskite system such as La_2VMnO_6. To date, however, there has been no successful experimental realization of an HM-AFM [15]. In this study, we search for candidates for HM-AFMs in double perovskites and thiospinels.

2.1. Double perovskite HM-AFM

It has been speculated that mixed-cation double perovskites of $AA'BB'O_6$-type might form ordered structures and provide good candidates for an HM-AFM [14]. The success in synthesizing the ordered La_2CrFeO_6 as an artificial superlattice of (111) layers of $LaFeO_3/LaCrO_3$ stimulates research on developing new double perovskites with exotic properties [16].

We have thus explored the $AA'BB'O_6$-type double perovskites to search for possible HM-AFMs. We have chosen $LaAVRuO_6$ (LAVRO: A = Ca, Sr and Ba) as potential candidates. In the ionic picture, V and Ru ion are expected to be trivalent V^{3+} ($3d^2$) and tetravalent Ru^{4+} ($4d^4$), respectively. Then V^{3+} ion has spin moment of 2 μ_B in high-spin state while Ru^{4+} ion has 2 μ_B in low-spin state, and so, if they are antiferromagnetically coupled, the total magnetic moment will be zero.

Indeed, the LSDA total densities of states (DOSs) of LAVRO (A = Ca, Sr, and Ba) in figure 1(A) show that all three systems have HM-AFM nature. LaAVRO with the antiferromagnetic coupling of V and Ru spins corresponds to a superlattice having a layered structure of stacking along the [111] direction, as in La_2CrFeO_6. The DOSs are similar for all LAVRO, even if the A-site atom is varied. The antiparallel alignment of Ru and V magnetic moments yields zero total magnetic moment for all cases. $LaSrVRuO_6$ has a ferrimagnetic



(A)

(B)

Figure 1. (A) The total DOSs of $LaAVRuO_6$ in the LSDA. (a) A = Ca, (b) A = Sr and (c) A = Ba. (B) The orbital projected DOS of $LaSrVRuO_6$. The solid and dotted curves in (a) and (b) denote t_{2g} and e_g states, respectively. (a) V 3d, (b) Ru 4d and (c) O 2p.

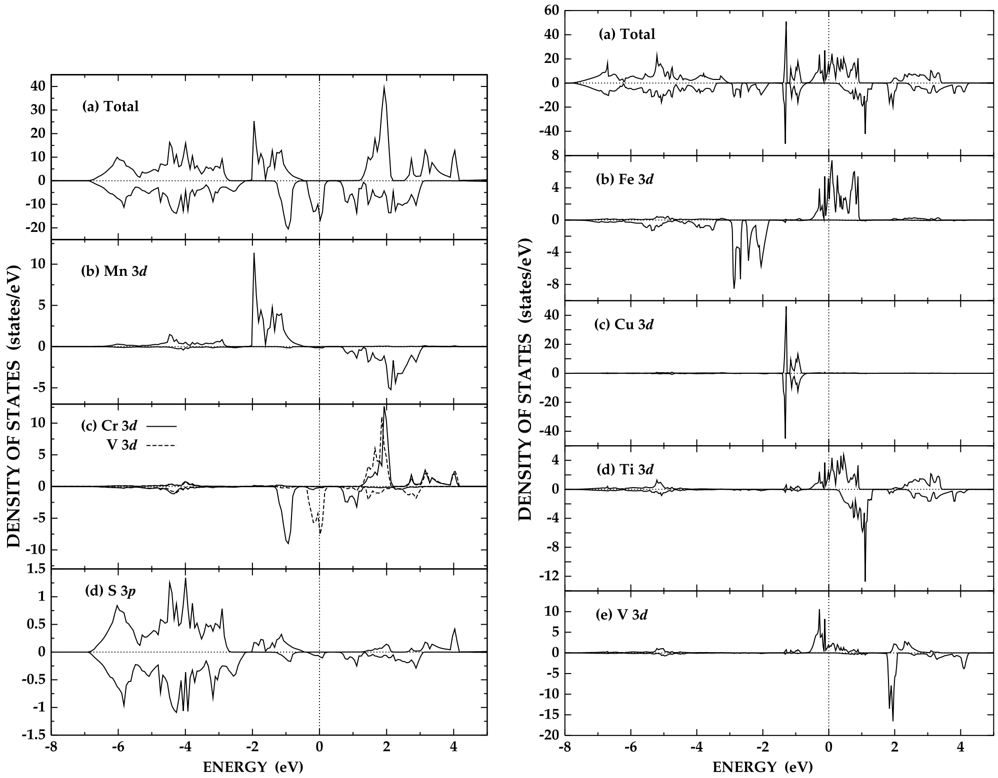
ground state which is lower in energy than the paramagnetic state by 0.24 eV/fu. Likewise, both $LaCaVRuO_6$ and $LaBaVRuO_6$ have ferrimagnetic ground states too. The LSDA + U + SO also yields the same results [17].

As shown in figure 1(B), for $LaSrVRuO_6$, an energy gap of ~0.8 eV opens between the occupied Ru t_{2g} and the empty V t_{2g} states in the spin-up bands. On the other hand, the spin-down bands are metallic and composed of t_{2g} states of Ru and V. It is likely that two valence states of V^{3+}/Ru^{4+} and V^{4+}/Ru^{3+} are nearly degenerate to produce a type of double exchange (DE) interaction [18]. That is, the hopping of itinerant t_{2g} spin-down electrons between Ru–V sites yields a kinetic energy gain so as to induce ferrimagnetism between Ru–V spins. This mechanism explains both the half-metallicity and the ferrimagnetism in $LaSrVRuO_6$.

2.2. *Thiospinel HM-AFMs*

Most of the thiospinel compounds of AB_2S_4-type (A, B: transition metals) with cubic structure have a ferrimagnetic ground state. Usually, the magnetic moment of the A ion in the tetrahedral site is antiferromagnetically polarized with that of the B ion in the octahedral site. Under this circumstance, there are some pairs of A and B which give rise to the exactly cancelled magnetic moment in AB_2S_4. Moreover, some spinels have HM electronic structures, as in $FeCr_2S_4$ [6, 19, 20]. Then, by choosing proper pairs which satisfy these two conditions, one can devise thiospinels with HM-AFM nature. In this work, we will propose two candidates for HM-AFMs in thiospinels with the cubic spinel structure: $Mn[CrV]S_4$ and $Fe_{0.5}Cu_{0.5}[V_{0.5}Ti_{1.5}]S_4$.

Figure 2(A) shows that $Mn[CrV]S_4$ has an HM-AFM ground state. The spins of Cr and V are ferromagnetically aligned, but they are antiferromagnetically aligned to those of Mn.



(A) (B)

Figure 2. (A) Total and projected local density of states (PLDOS) of Mn[CrV]S_4. (B) Total and PLDOS of $Fe_{0.5}Cu_{0.5}[V_{0.5}Ti_{1.5}]S_4$.

The energy gap is evident near E_F in the spin-up density of states (DOS), and the DOS at E_F originates mainly from the spin-down V 3d ($\sim t_{2g}^2$ electrons) states which will contribute to the metallic conductivity. The occupied DOS suggests that Mn[CrV]S_4 has a nominal valence configuration of $Mn^{2+}[Cr^{3+}V^{3+}]S_4^{2-}$, which corresponds to the normal spinel structure.

FeV_2S_4, if it exists in the cubic spinel form, would be a strong candidate for an HM-AFM[2]. On the other hand, V and Ti form thiospinels only with Cu: CuV_2S_4 and $CuTi_2S_4$ [21]. On the basis of this, we have explored the combination of Fe, Cu, V, and Ti to make a thiospinel possessing both HM and AFM nature: $Fe_{0.5}Cu_{0.5}[V_{0.5}Ti_{1.5}]S_4$ (FCVTS). We have performed an LSDA electronic structure calculation for FCVTS taking into account the ordered 1-V and 3-Ti configurations. As shown in figure 2(B), FCVTS really has an HM-AFM electronic structure. The DOS at E_F consists of the spin-up Fe e_g and V and Ti t_{2g} states. The nominal valence configurations of Fe and Cu are close to Fe^{2+} and Cu^{1+}, respectively. The ferrimagnetic mechanism in FCVTS can be understood in terms of the kinetic energy gain through the spin-polarized hopping between A and B sites, as in the case of $Fe_{0.5}Cu_{0.5}Cr_2S_4$ [6, 22].

3. Oxide-based DMSs

Oxide-based DMSs such as TM-doped ZnO [23] and TiO_2 [24, 25] have been reported to have T_C higher than room temperature. Recently, it has also been reported that Co-doped

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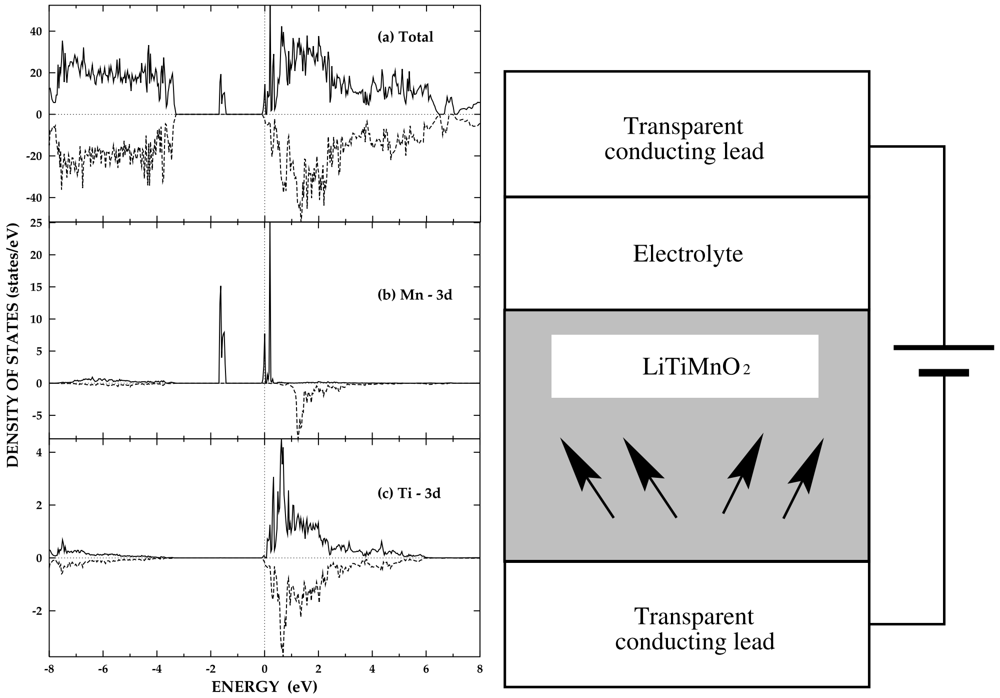
[2] FeV_2S_4 crystallizes in the hexagonal NiAs structure (Cr_3S_4-type).



(A) (B)

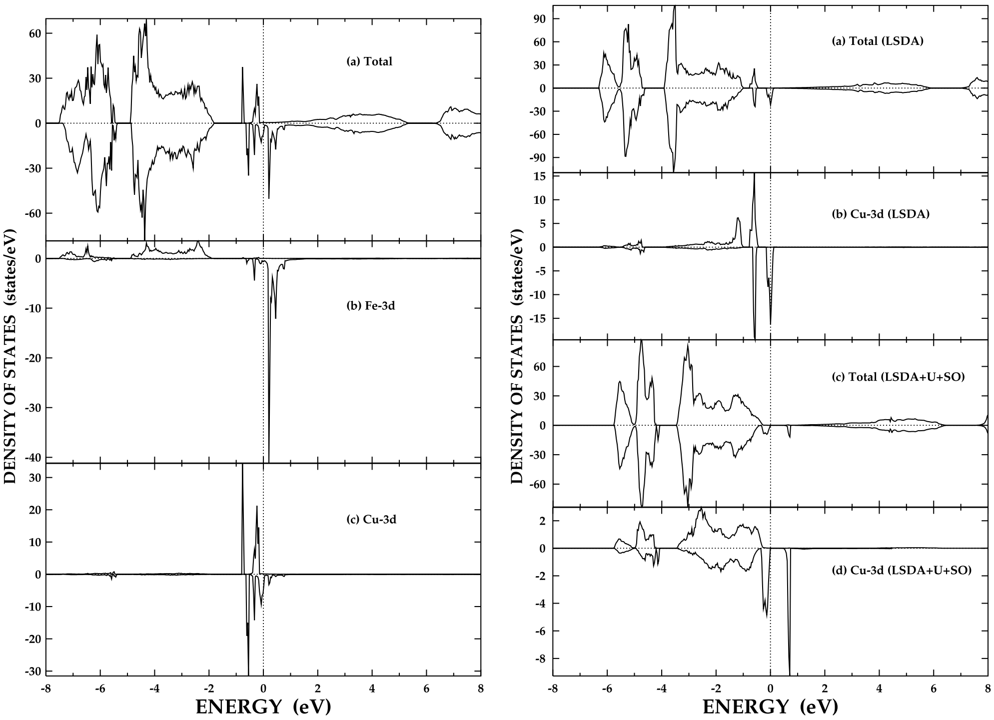
Figure 3. (A) The LSDA total and PLDOS for Li-intercalated $Ti_{0.9375}Mn_{0.0625}O_2$ (Li/Ti = 0.067). (B) Schematic diagrams for an electric-field controlled nonvolatile FM and an electrochromic device based on Li-intercalated Mn-doped TiO_2.

SnO_2 shows ferromagnetism with T_C as high as 650 K [26]. However, it is still controversial whether the FM features in these systems are intrinsic DMS properties or not. Therefore we employ additional intercalation and codoping methods to make oxide-based DMSs.

3.1. *Li-intercalated transition-metal doped anatase* TiO_2

Independently of the DMS project, Li intercalation in anatase TiO_2 has been studied extensively for possible uses in high energy density batteries, electrochromic, and solar-cell devices. Motivated by the easy Li intercalation into anatase TiO_2, we have explored the magnetic properties of TM-doped TiO_2 with intercalating Li. To this end, we have investigated electronic structures of Li-intercalated $Ti_{0.9375}Mn_{0.0625}O_2$. We have found that Mn-doped TiO_2 with sufficient intercalated Li concentration has metallic and ferromagnetic ground states, implying that n-type carriers produced by Li intercalation induce the ferromagnetism.

Figure 3(A) provides the LSDA density of states (DOS) for the FM phase of $Ti_{0.9375}Mn_{0.0625}O_2$ with Li/Ti = 0.067. We have obtained a metallic ground state, contrary to the non-intercalated Mn-doped TiO_2 which has an insulating ground state [27]. The Mn 3d projected local density of states (PLDOS) indicates the high-spin state of Mn. Most of the occupied Mn 3d(t_{2g}) states are located in the energy gap region, whereas the empty Mn 3d states are shifted up and hybridized with the Ti 3d conduction band. Thus the extra n-type carriers produced by Li intercalation fill not only the Mn e_g majority spin states but also the Ti 3d conduction band, indicating that the simple rigid band concept does not work. For higher Li concentration of Li/Ti = 0.133, we have also obtained magnetic and metallic ground states.



(A) (B)

Figure 4. (A) The LSDA total and TM 3d PLDOSs for $Zn_{0.875}Fe_{0.0625}Cu_{0.0625}O$ for an Fe–Cu separation of 3.2499 Å. (B) The LSDA and LSDA + U + SO ($U = 3.0$ eV) total and Cu 3d PLDOSs for $Zn_{0.9375}Cu_{0.0625}O$.

On the basis of above findings, we propose a new spintronic device which can be controlled by the electric field. Figure 3(B) shows a schematic diagram of a device made of Mn-doped TiO_2 operating by voltage bias. Li ions are supplied from the Li electrolyte. It is thus possible to control the carrier concentration and the consequent magnetic ordering artificially by the electric field. Even after removing the bias, magnetic ordering is maintained, unless a reversed bias is applied. In addition, if the optical property is not affected by doped TM elements as in the case of Co-doped TiO_2 [24], one can fabricate a multi-functional device with variable magnetic and electrochromic properties. That is, an electric-field controlled spintronic and electrochromic device can be realized based on the Li-intercalated TM-doped anatase TiO_2 system.

3.2. Ferromagnetism in Zn_{1-x} $(FeCu)_xO$

$Zn_{1-x}Co_xO$ films made by the pulsed-laser deposition technique were reported to have FM behaviour with T_C higher than room temperature [23]. However, the reproducibility was less than 10%. Hence the realization of FM long range order in Co-doped ZnO films is controversial. On the other hand, there was also a trial to make ZnO-based DMS by doping double TM elements (Fe, Cu) [28]. We have investigated the magnetic mechanism in (Fe, Cu) doped ZnO: $Zn_{0.875}(Fe_{0.5}Cu_{0.5})_{0.125}O$.

Figure 4(A) presents the LSDA DOS of $Zn_{0.875}Fe_{0.0625}Cu_{0.0625}O$ for an Fe–Cu separation of 3.25 Å. One can notice the strong hybridization between Fe and Cu 3d states. Further, some new states are seen in the Cu 3d minority spin PLDOS between e and t_2 with local d_{xy}-like characters. Cu 3d PLDOS has a reduced exchange splitting, manifesting the DOS characteristic of the low-spin state. In figure 4(B), the DOS of Cu-doped ZnO is presented for comparison. The LSDA for $Zn_{0.9375}Cu_{0.0625}O$ yields a stable FM and half-metallic ground state, while the LSDA + U + SO yields an insulating electronic structure with substantial orbital magnetic moment of 1.05 μ_B. The orbital moment is polarized in parallel with the spin moment (0.8 μ_B), and so the total magnetic moment amounts to 1.85 μ_B/Cu. The valence state of Cu in Cu-only doped ZnO corresponds to $Cu^{2+}(d^9)$.

Noteworthy from PLDOSs in figure 4 is that there occurs charge transfer from Fe to Cu, and accordingly Fe and Cu in $Zn_{0.875}Fe_{0.0625}Cu_{0.0625}O$ are likely to have nominal $Fe^{3+}(d^5)$ and $Cu^{1+}(d^{10})$ configurations, respectively. As a result, the electron occupancy at the Cu site increases, and so Cu has a reduced spin magnetic moment of 0.5 μ_B as compared to 0.8 μ_B in Cu-only doped ZnO. The charge transfer from Fe to Cu is expected to disturb the Jahn–Teller distortion at Cu sites and concomitantly make the system metallic [29]. Further, it will cause the mixed-valent states for Fe (Fe^{2+}–Fe^{3+}) and Cu (Cu^{2+}–Cu^{1+}) ions, and the consequent double-exchange-like interaction is expected to induce ferromagnetism in (Fe, Cu) doped ZnO.

4. Conclusion

We have proposed that the mixed-cation double perovskite LAVRO (A = Ca, Sr, and Ba) and thiospinel $Mn[CrV]S_4$ and $Fe_{0.5}Cu_{0.5}[V_{0.5}Ti_{1.5}]S_4$ are potential candidates for the HM-AFMs. A type of the double exchange interaction is operative in these systems to yield the half-metallicity and the antiferromagnetism.

We have also shown that the DMS of Mn-doped anatase TiO_2 can be synthesized by Li intercalation. We proposed a novel non-volatile spintronic and electrochromic multifunctional device which can be controlled by the electric field. For $Zn_{0.875}Fe_{0.0625}Cu_{0.0625}O$, the charge transfer between Fe and Cu causes mixed-valent states of Fe and Cu, and accordingly a type of double-exchange interaction is expected to induce ferromagnetism in (Fe, Cu) doped ZnO.

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