Density-functional study on the ferromagnetism of (Fe,Zr)-codoped In_2O_3

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Abstract. We have investigated the Fe and (Fe,Zr)-codoped In_2O_3 by first-principle calculations. Our results reveal that antiferromagnetic interaction dominates in the Fe-doped system. When Zr is introduced, the extra carriers mediate the interaction between defects and greatly enhance the ferromagnetism of the codoped system. The ferromagnetic interaction can be attributed to RKKY interaction.

1 Introduction

Recently, diluted magnetic semiconductors (DMS) abstract more and more attentions due to their potential applications into spintronics. DMS has both spin and charge degrees of freedom, which are more advanced for the design of nanodevices. Traditionally, DMS are fabricated by doping transition-metal elements into semiconductors. However, the clustering of magnetic elements and the second phase are usually formed between the crystalline boundaries, which masks the intrinsic ferromagnetism of the doped system.[1,2] Moreover, single element doping usually does not necessarily lead to the ferromagnetism. To overcome this problem, two elements codoping are proposed and tested in many experiments. Recently, Kim et al. reported that by doping Fe into In_2O_3, RT ferromagnetism can be obtained in the doped system.[3] Moreover, they found that ferromagnetism was enhanced by codoping Fe and Zr into In_2O_3.[4] However, the theoretical explanation is still absent and the underlying physics needs further exploration.

In this article, we investigated (Fe,Zr)-codoped In_2O_3 by first-principle calculations. The magnetism of the doped system with only Fe substitution is studied and the magnetic interaction between defects is calculated. Particularly, we calculated the magnetic interaction for the system when Fe and Zr substitutions occur spontaneously. The enhancement of ferromagnetism in the codoping system is found and the underlying physics is discussed.

2 Methods

The supercell of $In_{32}O_{48}$was built from the unit cell with group symmetry of I213. Possible sites for Fe and Zr substitutions are labeled. We use the full-potential linearly augmented plane waves plus local orbital methods as implemented into WIEN2K Computing package, to investigate the magnetic properties of the doped system.[5] The waves inside the atomic spheres are expanded by harmonic spherical functions up to l=10. The waves in interstitial regions are expanded by plane waves. The maximum cut off of plane wave expansion is set by $R \bullet K_{\max} = 7.0$ .We use the generalized-gradient-approximation of Perdew-Burke-Ernzerhof form for the exchange-correlation potential.[6]

3 Results

By introducing one Fe impurity to the supercell, we investigate the magnetic properties of the doped system with the concentration of 3.125%. Both the spin-polarized and nonmagnetic states are calculated. Our results reveal that the system favors the spin-polarized state, which is 1.6 eV in energy lower than the nonmagnetic state. Total moments of 5.00 μ_B are induced in the supercell by doping

one Fe atom. The local moment of Fe is 3.97 μ_B, which agrees with the results of other groups, and the oxygen atoms nearest to Fe impurity is 0.11 μ_B. The valence of Fe ion is 3+ and the electronic configuration of d shell is $e^2_{g\uparrow} t^3_{2g\uparrow}$. Fe impurity couples to its nearest oxygen atoms ferromagnetically. Negligible moments are also induced in In atoms and they couple to the nearest oxygen atoms ferromagnetically.

To further investigate the magnetic properties of the doped system, we calculate the total and projected density of states (DOSs) for $In_{31}FeO_{48}$ and list them in Fig. 1.

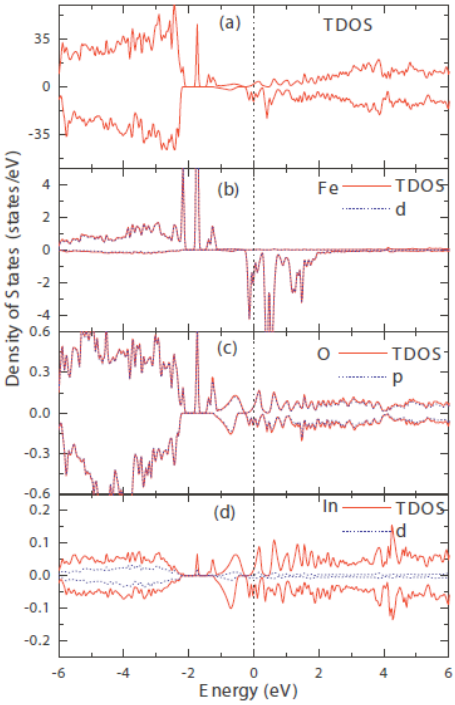

Fig. 1: Total and projected density of states for the supercell of $In_{31}FeO_{48}$. (a) Total DOSs. (b) d, d_{xy} and d_{yz} DOSs for Fe. (c) Total and p-DOSs for the oxygen atom nearest to Fe. (d) Total and d-DOSs for In.

It is noticed that two peaks emerge for the majority states and the Fermi level crosses one peak, which means a few carriers are introduced to the system. The two peaks near the Fermi are introduced by d_{xy} and d_{yz} orbitals of Fe, which hybridize with the p orbital of oxygen heavily. At the Fermi level, weak hybridization also occurs for In atoms, whose magnitude is negligible compared to that of Fe and O atoms.

To investigate the magnetic coupling between the impurities, we introduce two Fe impurities to the supercell, which corresponds to the impurity concentration of 6.25%. Different structures are generated by changing the distance between impurities. Both ferromagnetic and antiferromagnetic states are calculated. We define the magnetization energy, $\Delta E_M = E_{AF} - E_{FM}$, to indicate the magnetic states of the doped system. A positive value means the ferromagnetic state is more stable and vice versa. The magnetization and the total moments induced are listed in table I.

Table 1: Magnetization energy ΔE_M and the total moments M_{cell} of the ferromagnetic state for different configurations. *d* is the distance between two impurities.

Cinfigurations	*d* (Å)	ΔE_M (meV)	M_{cell} (μ_B)
(C1,C2)	3.40	-48.4	10.0
(C1,C3)	5.14	-28.7	10.0
(C1,C4)	6.16	-6.5	10.0
(C1,C5)	7.27	-3.5	10.0
(C1,C6)	8.91	1.6	10.0

It is noticed that the AF state is predominated in the systems and the magnetization energy decays fast as the distance decreases. Although our results are considerably less than those in Ref.[ ], the decaying trend qualitatively agrees with it. Thus the FM state should be absent for the system with Fe substitution only.

Traditionally, the ferromagnetism can be mediated by increasing the carrier density via codoping. Experimentally, robust ferromagnetism was also reported in (Fe,Zr)- or (Fe,Cu)-codoped In_2O_3. In our calculations, magnetization energy of the systems with two Fe and one Zr impurities occupying different positions is investigated and the results are listed in table 2.

The total moments decrease to 9.0 μ_B due to one additional electron introduced by Zr. The local moments of Fe decreases to 3.85 μ_B. It is found that Zr has vanishing local moments, which means the additional electron of Zr is transferred to Fe impurities. Compared to the mediation of oxygen vacancy, the ferromagnetic coupling occurs between Fe impurities with nearer distance and the antiferromagnetic coupling is greatly weakened. To further study the magnetic properties of (Fe, Zr)-codoped system, we plot the total and projected DOSs in Fig. 2 for the configuration of In_{Fe}(C1,C3)+ In_{Zr}(C2).

Table 2: Magnetization energy for the configurations of (Fe,Zr)-codoped In_2O_3

Configurations	ΔE_M (meV)	M_{cell} (μ_B)
In_{Fe}(C1,C2)+ In_{Zr}(C7)	15.2	9.0
In_{Fe}(C1,C3)+ In_{Zr}(C2)	14.8	9.0
In_{Fe}(C1,C4)+ In_{Zr}(C3)	13.3	9.0
In_{Fe}(C1,C4)+ In_{Zr}(C2)	10.5	9.0
In_{Fe}(C1,C5)+ In_{Zr}(C3)	-7.7	9.0
In_{Fe}(C1,C5)+ In_{Zr}(C2)	-1.5	9.0
In_{Fe}(C1,C6)+ In_{Zr}(C2)	-6.8	9.0

It is noticed that the Fermi level is shifted upwards and consequently the minority states of Fe is occupied. The 3d orbital of Zr is almost empty, which is consistent with the zero local moments. Since the Fermi level crosses both the 3d states of Fe and the 2p states of O, the ferromagnetism may arise from the RKKY interaction.

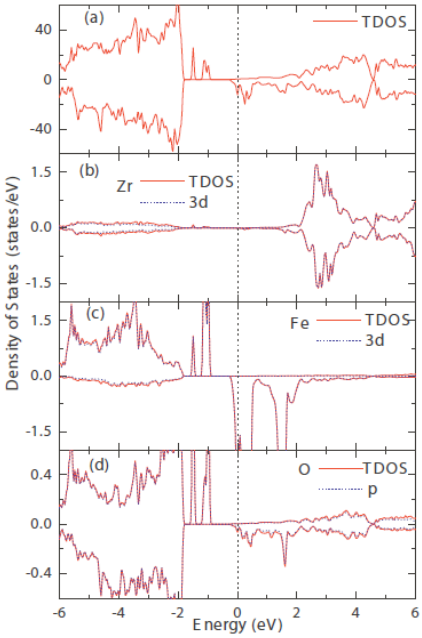

Fig. 2: Total and projected density of states for the supercell of In_{Fe}(C1,C3)+ In_{Zr}(C2). (a) Total DOSs. (b) Total and projected 3d-DOSs for Zr. (c) Total and 3d-DOSs for Fe. (d) Total and p-DOSs for the oxygen atom nearest to Fe.

4 Conclusions

We have investigated the (Fe,Zr)-codoped In2O3 by first-principle calculations. Our results reveal that only Fe substitution does not lead to the ferromagnetism of the doped system. When Zr is introduced, the extra carriers are introduced to the doped system and lead to RKKY interaction. Our results reveal that (Fe,Zr)-codoing can greatly enhance the ferromagnetism of the doped system.

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