First-principle study on the ferromagnetism of Fe-doped In_2O_3

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Abstract. Recent experiments reveal that strong ferromagnetism can be obtained in Fe-doped In_2O_3 films. However, the underlying physics is not well understood. By density-functional calculation, we systematically study the magnetic properties of Fe-doped In_2O_3 mediated by intrinsic vacancy. Our results reveal that charge transfer strongly depends on the position of defect, which consequently affects the magnetic coupling of the system. The ferromagnetism can be attributed to the RKKY interaction.

1 Introduction

Recently, diluted magnetic semiconductors (DMSs) have attracted much attention due to their potential applications in spintronics. By exploring both spin and charge degrees of freedom, DMSs are promising to integrate the data processing and storage and can greatly facilitate computer technology. Traditionally, DMSs are fabricated by doping transition-metal (TM) into semiconductors. For example, room-temperature ferromagnetism has been reported in Fe, Co or Ni doped ZnO, SnO_2 or TiO_2.[1,2] Due to the low solubility of TM in these host semiconductors, the clustering or the formation of secondary phases of TM is often considered as the origin of ferromagnetism in the doped systems. Nevertheless, there are still many reports on the ferromagnetism in TM-doped semiconductors without detected impurity agglomerations. It seems that TM impurities do not lead to ferromagnetism directly and the ferromagnetism is often related to the presence of intrinsic vacancies. For instance, ferromagnetism has been reported in the TM-doped semiconductors of oxide under oxygen-poor condition. However, the formation of intrinsic vacancy mainly depends on the preparing condition and the precise concentration of intrinsic vacancy is hard to control. It is also found that ferromagnetism can be greatly affected by carrier density, which can be adjusted by codoping. Experimentally, by codoping TM and other elements into semiconductors, ferromagnetism was observed to be enhanced in many codoped semiconductors.[3,4] However, there are still negative reports on the ferromagnetism adjusted by codoping and the mechanism of impurity mediation as well as the underlying physics is still not clear.

In this article, we reported our theoretical study on the magnetic properties of Fe-doped In_2O_3. Our results reveal that charge transfer strongly depends on the position of vacancy, which consequently affects the magnetic coupling of impurities. Oxygen vacancies can greatly enhance the substitution of Fe in In_2O_3 and mediate the interaction between defects. Our results reveal that the oxygen vacancies can effectively tune the doped system into ferromagnetic phase.

Methods

A supercell of $In_{32}O_{48}$ is built from the unit cell with space group symmetry of I213. By substituting In and O atoms with impurities and vacancies, different configurations are generated. The structure of the supercell with possible sites for substitution is shown in Fig. 1. 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. The radii of muffin-tin spheres for In, Fe, Zr and O are set to be 2.10, 2.00, 2.16 and 1.60 Bohr respectively. The angular parts of waves inside the atom spheres are expanded by harmonic spherical functions up to l=10. In the interstitial regions, the waves are expanded by plane waves, which are cut off by setting $R \cdot K_{max}$=7.0. The generalized-gradient-approximation of Perdew-Burke-Ernzerhof form is used for the exchange-correlation potential.[5] A $4\times4\times4$ k-mesh is generated for the Brillouin zone integration.

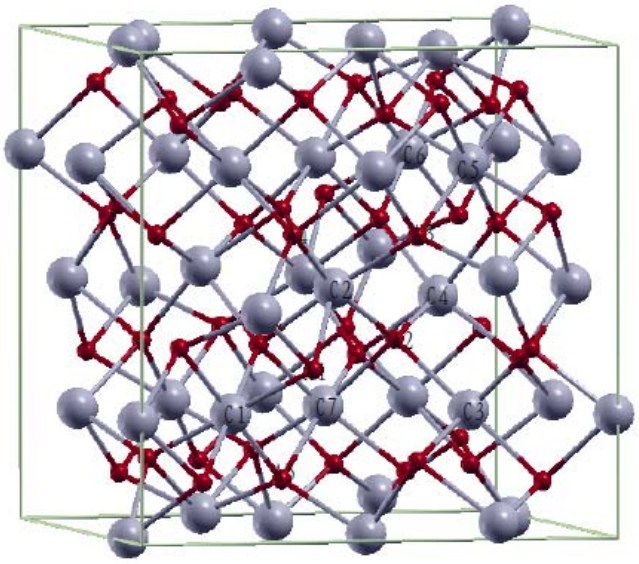

Fig. 1: Supercell structure of $In_{32}O_{48}$. The grey and red shperes represent In and O atoms respectively. Possible sites for the substitutions of Fe and O vacancies are labeled by C1-C7 and A1-A5 respectively

Results

Generally, the intrinsic vacancies play an important role in the mediation of ferromagnetism in TM-doped semiconductors. In our calculations, the mediation of both anion and cation vacancies are investigated and the results are shown in table 1. For the case of one oxygen vacancy, most systems have the total moments of 10.0 μ_B . This means the charges of vacancy are localized and do not transfer to the Fe impurities, and consequently most systems still have antiferromagnetic ground states. This is consistent with the result of previous calculation. Previous calculations reported that ferromagnetism was found in the system with Fe-V_O-Fe configuration. However, our calculations reveal that the Fe-V_O-Fe configuration does not necessarily lead to ferromagnetism. For example, neither the configuration of In_{Fe}(C1,C2)+V_O(A1) nor the configuration of In_{Fe}(C1,C7)+V_O(A5) has the ferromagnetic ground state. We notice that the distance of 3.57 Å between impurities in our relaxed system is considerably less than the value about 4.0 Å in the previous calculations. Since the distance between impurities has significant effect on the magnetism of the system, especially for the case of neighbor impurities. Therefore, the discrepancy may arise from the different distance between impurities. For the configuration of In_{Fe}(C1,C6)+V_O(A1), the total moments decrease to 9.1 μ_B and ferromagnetism is enhanced. This means the charges of vacancy transfer to the Fe impurities and consequently the total moments are reduced. Note that the ferromagnetism is also strongly dependent on the position of oxygen vacancy. When two oxygen vacancies are introduced into the systems, both ferromagnetism and antiferromagnetism are enhanced. The total moments are further reduced to 8.0 μ_B . For the case of In vacancy mediation, the total moments are largely reduced due to the removal of 3d electrons from Fe impurities. However, the magnetic states are strongly dependent on the position of In vacancy and in most cases the antiferromagnetism is dominant.

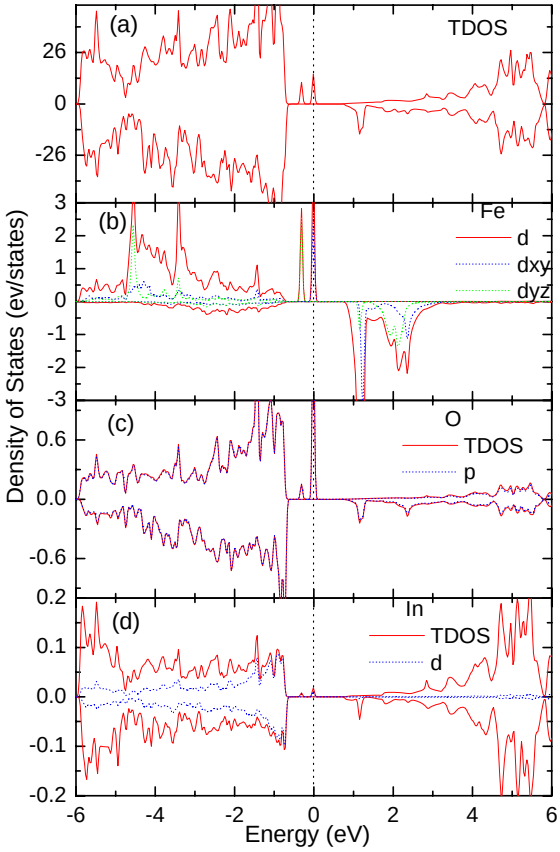

Fig. 2: Total and projected density of states for the supercell of In_{Fe}(C1,C5)+V_O(A1,A2). (a) Total DOSs. (b) Total and 3d DOSs for Fe. (c) Total and p-DOSs for the oxygen atom nearest to Fe. (d) Total and d-DOSs for In.

To further investigate the magnetic properties of the system, we plot the total and projected density of states of the configuration of In_{Fe}(C1,C5)+V_O(A1,A2) in Fig. 2. It is noticed that the Fermi level is shifted upwards and the electrons begin to occupy the minority 3d states of Fe impurity. This means the charges of oxygen vacancies do transfer to the Fe impurities. The local moments of Fe impurity decreases from 3.97 to 3.58 μ_B . Note that the Fermi level crosses the bottom of conduction band, which means the ferromagnetism may arise from the RKKY interaction by itinerant electrons.

Table 1: Magnetization energy for different configurations with vacancy. M_{cell} is the total moments of the system in ferromagnetic state.

Configurations	ΔE (meV)	M_{cell} (μ_B)
In_{Fe}(C1,C2)+V_O(A1)	-79.3	10.0
In_{Fe}(C1,C3)+V_O(A1)	-17.2	10.0
In_{Fe}(C1,C4)+V_O(A1)	-12.6	10.0
In_{Fe}(C1,C5)+V_O(A1)	-6.5	10.0
In_{Fe}(C1,C6)+V_O(A1)	17.3	9.1
In_{Fe}(C1,C5)+V_O(A2)	-11.1	10.0
In_{Fe}(C1,C5)+V_O(A1,A2)	50.5	8.0
In_{Fe}(C1,C5)+V_O(A2,A4)	79.1	8.0
In_{Fe}(C1,C4)+V_O(A1,A3)	-45.8	8.1

Conclusions

We have investigated the magnetic properties of Fe-doped In_2O_3 by first-principle calculations. Our results reveal that the AF coupling dominates in the Fe-doped In_2O_3 if the vacancies do not be

considered. However, when the oxygen vacancy is introduced, the ferromagnetism arises from the RKKY interaction. Oxygen vacancies can greatly enhance the ferromagnetism of the doped system.

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