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Stable dilute magnetic semiconductor and Curie temperature of 3*d* transition metal doped strontium titanate perovskite material

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ABSTRACT

Electronic properties and ferromagnetic (FM) state of transition metal (TM) doped strontium titanate $SrTiO_3$ (STO) dilute magnetic semiconductors (DMS) have been investigated using the Korringa-Kohn-Rostoker (KKR) Green's function method. The perovskite type alloys $Sr(Ti_{1-x}D_x)O_3$ exhibit stable FM state with V, Cr, Fe, and Co doped cases, whereas spin glass (SG) state is found with Mn doped case. Here *D* is the 3*d* TM element and *x* is the fractional concentration of *D* in the range of $x = 0.01–0.35$. Crystal field splitting of 3*d* electronic states induces magnetic properties into the TM doped STO compounds. Low T_C has been found for V, Cr, and Co doped compounds, wherein Fe doped STO shows T_C above room temperature for typical concentrations with $x > 0.08$. Calculated T_C in Fe doped STO agrees well with the experimental data. Besides, T_C increases with TM concentrations and follows the pattern of square root of doping concentrations at the region of $x < 0.1$. The uncompensated density of states at the Fermi level are responsible for occurring FM state in the calculated alloys.

1. Introduction

Dilute magnetic semiconductor (DMS) [1] is a fascinating field of research for its wide usage in spintronic devices as an emergent materials with high performance. DMSs are usually designed by introducing transition metal (TM) impurities into the non-magnetic semiconductors. These materials are interesting from the point of view of applications, because spintronic materials are small in size and having innovative features in modern electronic devices.

Strontium Titanate, $SrTiO_3$ (STO), a perovskite semiconductor, has mixed ionic and covalent bondings properties. This nature of chemical bonding leads to a unique crystal structure, which makes it a model electronic and spintronics material [2]. Magnetic and electronic properties in STO are usually related to unfilled 3*d* electron shells of TM ions incorporated in the Ti site. These features open up the possibility that the magnetic behavior of the materials can be controlled simply by changing the carrier density. Though a considerable amount of experimental data have been already accumulated, the theoretical understanding of high T_C DMS are still in a preliminary stage.

Recently, Itoh group found ferroelectric properties in $SrTiO_3$ by isotope exchange of ^{18}O with ^{16}O without introducing a random field by the cation substitution or applying any external fields [3]. Coey et al. reported an experimental study of inducing magnetic moment in perovskite STO by surface defect with tiron ($C_6H_4Na_2O_8S_2$) that forms a strong complex with Ti at the surface [4]. Rice team found optically induced magnetism by creating slight oxygen deficiency in bulk STO crystals using magnetic circular dichroism (MCD) spectroscopy and superconducting quantum interference device (SQUID) magnetometry [5]. Kumar et al. investigated the Fe^{4+} doped $SrTiO_3$ film and reported ferroelectric properties with a high transition temperature ($T > 200\,^{\circ}C$) [6]. Moetakef group also reported that La- doped $SrTiO_3$ films and $GdTiO_3/SrTiO_3$ heterostructures exhibit ferromagnetism at low temperature [7]. Biasi and Grillo investigated electron magnetic resonance of Cr^{3+} doped STO samples at Ti site and found that the line width of the resonance spectrum increases with increasing of Cr concentration [8].

To improve the magnetic properties of doped STO, several research groups attempted to dope with TM ions such as Mn^{3+}, Fe^{3+}, and Co^{2+} at the Ti site of the host material [9–11]. Most of the afforts have been given to understand the magnetic behavior of these systems, which are based on the local magnetic moments interaction with each other via Ruderman-Kittel-Kasuya-Yosida (RKKY) technique [12]. In RKKY interaction, second-order perturbation theory is used to describe the indirect exchange coupling. We have calculated the electronic structure of $Sr(Ti_{1-x}D_x)O_3$ by Korringa-Kohn-Rostoker (KKR) Green's function method, where *D* is the 3*d* TM atoms and *x* is the fractional concentration of *D*. In the present research, we have designed numerically ferromagnetic (FM) material based on the host STO semiconductor and

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calculated the stable FM state and T_C for different 3*d* TM atoms doped at Ti sites for seeking new spintronic materials.

In this article, we have presented the magnetic properties and electronic density of states (DOS) to seek the stability of FM phase in the perovskite type DMS $Sr(Ti_{1-x}D_x)O_3$. The total energy per unit cell of FM state and SG state have been calculated to estimate T_C using the mean field approximation (MFA). Magnetic moments pointed in one direction is considered as FM state. On the other hand, magnetic moments which are distributed randomly with zero net magnetization is defined as SG state. The FM state is stable when its energy is relatively lower than the energy of SG state. The mechanisms behind the FM stability was explained using the DOS and electron coupling between the orbitals.

The article is organized in the following way: in section 2, the methods of calculation is described briefly. The magnetic phase stability, net magnetic moment, local spin moment, FM transition temperature T_C, and DOS of perovskite type DMS are presented and discussed in section 3. Graphical presentations of the calculated results are shown and explained in this section. The results are summarized briefly in section 4.

2. Computational details

We have performed the first-principles electronic structure calculations, which is based on the KKR-Green's function method [13–18]. Exchange correlation (XC) energy functional is approximated using the generalized gradient approximation (GGA) [19,20] for calculation of electronic states. Magnetic disorder is handled using the coherent potential approximation (CPA) [21]. In the CPA scheme, configuration averaged properties of alloys are calculated within a single-site approximation. Therefore, we can simulate arbitrary concentrations of impurities without using a large supercell. The shape of the crystal potential is approximated by muffin-tin potential. We assume that the potential is spherically symmetric inside the atomic sphere and constant in the interstitial areas. Besides, scaler relativistic approximation (SRA) is used in the calculation. At room temperature, STO crystallizes in the ABO_3 simple cubic perovskite structure of space group *Pm*-3m (group number 221). The unit cell of perovskite STO structure is shown in Fig. 1(a). The indirect band gap energy of STO is 3.25 eV and direct band gap energy is 3.75 eV [2,22]. The lattice constant of the host STO compound is 0.3905 nm [23], which is used in the calculations. Local lattice distortion is neglected and experimental lattice constants of pure STO is used in the calculations. Electronic wave functions are considered with the angular momentum quantum number up to $\ell = 2$ at each atomic site. The Brillion zone is sampled with 286 k sampling points. Throughout the present calculations, we have used the KKR-CPA package, MACHIKANEYAMA-2000, developed by Akai [24,25].

3. Results and discussion

We have investigated the stability of FM state and T_C in compounds $Sr(Ti_{1-x}D_x)O_3$ with TM impurities in the range of $x = 0.01$–0.35, where *D* indicates V, Cr, Mn, Fe, Co and Ni atoms. The FM state can be described as $Sr(Ti_{1-x}D_x^{\uparrow})O_3$, where one directional arrow denotes the alignment of magnetic moments in the same direction and inducing a saturated magnetic moment in the compounds system. In this case, *d* electrons hybridize with the *p* electrons of the host STO [26]. On the other hand, SG state is described as $Sr(Ti_{1-x}D_{\frac{x}{2}}^{\uparrow}D_{\frac{x}{2}}^{\downarrow})O_3$, where the bi-directional arrows indicate the random orientation of magnetic moments such that the net magnetization is zero. We have calculated the total energy (TE) difference between FM and SG states as ΔE = TE (SG)–TE(FM) for estimating T_C.

Thorough analysis of the magnetic states of STO based DMS is shown in Fig. 1(b), which represents the calculated total energy difference in mRy against concentrations of TM atoms. Here dotted zero line is the separator between FM and SG states and the solid (dashed) line illustrates the energy difference for 10% (5%) concentrations of impurity in the doped systems. The positive energy difference signifies the stable FM state and negative energy difference indicate the SG state. One noticeable point here is that FM state is favoured in V, Cr, Fe and Co doped STO cases, whereas only Mn doped case exhibits lower energy situation in SG state. Valant et al. reported SG state for $SrTiO_3$ doped with 5% Mn in Ti site [27]. Choudhury et al. experimentally observed glassy state in Mn doped STO, which agree well with our calculated results [28]. On the contrary, no evidence of magnetic behavior is found in Ni doped STO compounds in the concentration range of $x = 0.01$–0.1.

The Hamiltonian in the Heisenberg spin model can be written as $H = -\sum_{i \neq j} J_{ij} \vec{s_i} \cdot \vec{s_j}$, where $\vec{s_i}(\vec{s_j})$ is the spin at site i(j) and J_{ij} is the exchange coupling constant between i and j sites [31–33]. In MFA, the correlations between neighboring spins are neglected, which can be expressed as $< s_i s_j > \approx < s_i > < s_j >$, where $< s_i s_j >$ express the correlations between neighboring spins and is approximated to independent spin entity. Since all the spins are identical, they all have the same expectation value $< s_i > = < s_j > = M$ for all sites i and j, where M is magnetization parameter. Therefore, in the MFA, a spin experiences an effective field consisting of the actual field plus an interaction with each of the neighboring spins by its average value. The central expression, $\kappa_B T_C = \frac{2}{3x}\Delta E$ is used to estimate T_C in the present study [34]. The calculated T_C and magnetic moments are shown in Table 1. However, the spin model has already been applied to calculate magnetic states and Curie temperature in DMS by Turek et al. [35] and Bouzerer et al. [36].

Estimated T_C in Kelvin against impurity concentrations of V, Cr, Fe and Co is shown in Fig. 2(a, b, c, d). In the low concentration range $x = 0.01$–0.1, T_C increases sharply with the increase of the

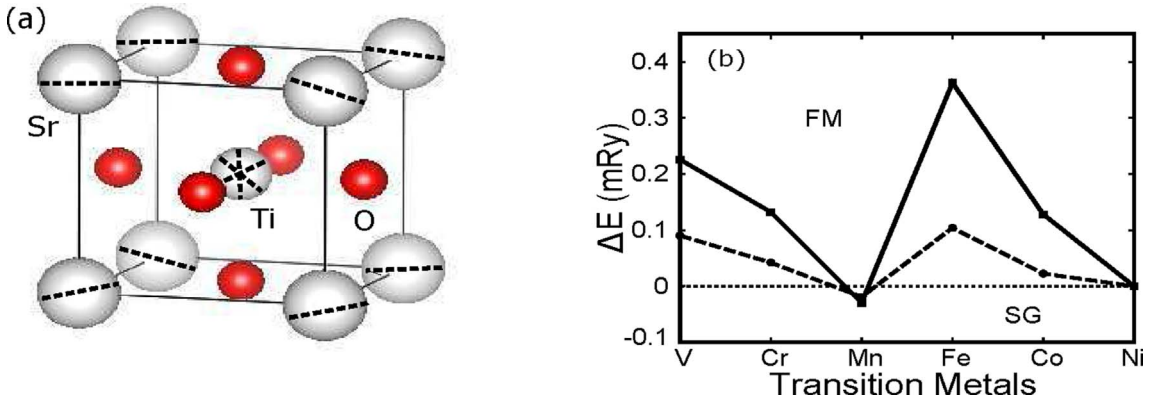

Fig. 1. (a) Unit cell of perovskite $SrTiO_3$ structure, (b)the energy difference (ΔE) per unit cell of $Sr(Ti_{1-x}D_x)O_3$ between the FM and SG states. The solid (dashed) line is plotted for 10% (5%) concentration of *D* atoms.