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Article

The melilite-type compound $(Sr_{1-x},A_x)_2MnGe_2S_6O$ (A = K, La) being a room temperature ferromagnetic semiconductor

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The seeking of room temperature ferromagnetic semiconductors, which take advantages of both the charge and spin degrees of freedom of electrons to realize a variety of functionalities in devices integrated with electronic, optical, and magnetic storage properties, has been a long-term goal of scientists and engineers. Here, by using the spin-polarized density functional theory calculations, we predict a new series of high temperature ferromagnetic semiconductors based on the melilite-type oxysulfide $Sr_2MnGe_2S_6O$ through hole (K) and electron (La) doping. Due to the lack of strong antiferromagnetic superexchange between Mn ions, the weak antiferromagnetic order in the parent compound $Sr_2MnGe_2S_6O$ can be suppressed easily by charge doping with either p-type or n-type carriers, giving rise to the expected ferromagnetic order. At a doping concentration of 25%, both the hole-doped and electron-doped compounds can achieve a Curie temperature (T_c) above 300 K. The underlying mechanism is analyzed. Our study provides an effective approach for exploring new types of high temperature ferromagnetic semiconductors.

1. Introduction

Magnetic semiconductors have been a research focus for a long time due to the expectation of simultaneously utilizing charge and spin degrees of freedom of electrons to achieve entirely new functionalities [1–4]. Diluted magnetic semiconductors (DMSs) are a representative family of magnetic semiconductors, which are nonmagnetic semiconductors doped with magnetic dopants. As model systems of DMSs, Mn-doped $A^{II}_{1-x}Mn_xB^{VI}$ alloys [5] and $A^{III}_{1-x}Mn_xB^{V}$ compounds [6], which were inspired by the motivation of introducing local moments into well-understood nonmagnetic semiconductors to make them ferromagnetic (FM) [7,8], have attracted extensive attentions. In the Mn-doped $A^{II}_{1-x}Mn_xB^{VI}$ alloys, the valence of the Mn^{2+} ions matches that of the cations, which allows them to be easily prepared in bulk form. Nevertheless, the early attempt at charge doping, either p-type or n-type, was difficult and the antiferromagnetic (AFM) superexchange dominates the magnetism of the $A^{II}_{1-x}Mn_xB^{VI}$ alloys, until the emergence of ferromagnetism at very low temperatures owing to the latter progress in charge doping [9]. On the other hand, the major obstacle in making III-V semiconductors magnetic is the low equilibrium solubility of Mn in the compounds [1,6]. The successful application of non-equilibrium epitaxial growth technique on the III-V based DMSs allows the solubility of Mn in $A^{III}_{1-x}Mn_xB^{V}$ films to exceed its equilibrium limited solubility. Subsequently, hole-induced ferromagnetic order in p-type (In,Mn)As was reported by Ohno et al. [10]. And the most widely studied (Ga,Mn)As has achieved a Curie temperature T_c of 200 K [11]. However, the great challenge for the ultimate goal to obtain ferromagnetic DMSs working at room temperature still stands.

Recently, Mn doped I-II-V compound Li(Zn,Mn)As [12], II-II-V compound $(Ba,K)(Zn,Mn)_2As_2$ [13], and III-VI-II-V compound (La,Ba)O(Zn,Mn)As [14], which are respectively isostructural to the related iron-based superconductors LiFeAs [15], $BaFe_2As_2$ [16], and LaOFeAs [17], were reported as new types of DMS materials. In these compounds, the spin doping and charge doping are decoupled and both can reach their respective appropriate concentrations. Meanwhile, they can be prepared as bulk samples effectively [12–14]. Noteworthily, the T_c of $(Ba_{0.7}K_{0.3})(Zn_{0.85}\,Mn_{0.15})_2As_2$ even reaches 230 K [18], higher than the record value achieved in (Ga,Mn)As [11]. However, for all these compounds together with the $A^{II}_{1-x}Mn_xB^{VI}$ alloys and the $A^{III}_{1-x}Mn_xB^{V}$ compounds, the cation sites (Zn or Ga) for spin doping locate in the tetrahedral crystal field of anions (such as As) and each cation site can connect with its nearest- and sometimes next-nearest-neighbor cation sites by bridging anions directly (Fig. 1a and 1b). Thus, the doped

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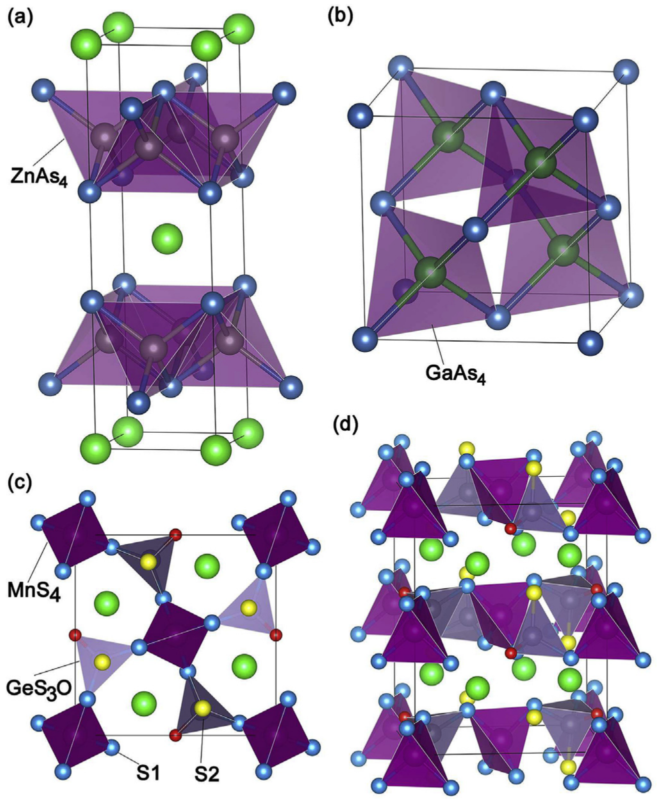

Fig. 1. (Color online) The schematic diagrams of crystal structure. Side views for (a) $BaZn_2As_2$ and (b) GaAs, in which the $ZnAs_4$ ($GaAs_4$) tetrahedra connect directly with each other. Top view (c) and side view (d) for $Sr_2MnGe_2S_6O$, in which the MnS_4 tetrahedra are separated by the GeS_3O tetrahedra.

Mn^{2+} ions, which replace the cations, may form Mn-Mn pairs bridged directly by anions (indeed true in the experiments [12–14]) so as to be antiferromagnetically coupled through superexchange interactions favorably in energy [19–22]. This induces the reduction of the net average magnetization for the Mn^{2+} ions and is harmful to the improvement of sample quality. On the other hand, for all these compounds, the FM order appears only when the charge doping is introduced, demonstrating that the ferromagnetism is induced by itinerant carriers [9,10,12–14]. Based on the above facts, searching for such a material, in which the nearest-neighbor AFM coupling is avoided and the effective charge doping can be achieved, may serve as an effective approach for exploring more feasible magnetic semiconductors [23].

In addition, the melilite-type oxide $Sr_2MnGe_2O_7$ [24] and oxysulfide $Sr_2MnGe_2S_6O$ [25] were successfully synthesized in experiments and reported as weakly AFM insulators with respective magnetic transition temperatures being only 4.4 and 15.5 K. Structurally, in both compounds, the MnO_4 (MnS_4) tetrahedra are separated by the GeO_4 (GeS_3O) tetrahedra (Fig. 1c and 1d) and the Mn atoms are distributed uniformly at a moderate separation of 5.86–6.73 Å [24,25]. This provides a great opportunity to block the possible nearest-neighbor AFM superexchange. Moreover, the sandwiched Sr atoms (Fig. 1d) act as charge reservoir layers similar to the Ba atoms in $BaZn_2As_2$ (Fig. 1a), which is promising for a feasible charge doping. Inspired by the rising of FM order in all previous DMSs via introducing itinerant carries [9,10,12–14], we infer that the charge doping may readily suppress the weak AFM order and further induce the ferromagnetic order in these melilite-type compounds.

In this work, we systematically studied the magnetic properties and electronic structures of the charge-doped oxysulfide $Sr_2MnGe_2S_6O$ as a model system for the melilite-type compounds by using density functional theory (DFT) calculations. We find that the charge doping, either *p*-type or *n*-type, can suppress the AFM order in the parent compound and then raise the FM order in the doped compounds $(Sr_{1-x},K_x)_2MnGe_2S_6O$ and $(Sr_{1-x},La_x)_2MnGe_2S_6O$. With a carrier concentration of 25%, typically the one in the previous DMS material $(Ba_{1-x}K_x)(Zn_{1-y}Mn_y)_2As_2$ [13], the $(Sr_{0.75},A_{0.25})_2MnGe_2S_6O$ (A=K, La) compound can achieve a Curie temperature T_c above 300 K. The rigid shifts of the band structures after doping show the semiconductor characteristics. Our theoretical prediction on this new type of room temperature ferromagnetic semiconductors calls for experimental validation.

2. Computational details

The spin-polarized density functional theory (DFT) calculations were carried out by using the projector augmented wave (PAW) method [26,27] as implemented in the Vienna Ab initio Simulation Package [28–30]. The generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) was employed for the exchange-correlation functional [31]. The kinetic energy cutoff of the plane-wave basis was set to be 520 eV. The space group of $Sr_2MnGe_2S_6O$ is $P\bar{4}2_1m$ [25]. In order to describe different magnetic configurations, we chose a supercell containing 48 atoms by doubling the tetragonal cell along *c*-direction as shown in Fig. 1d. To simulate the hole-type or electron-type doping, a part of Sr atoms were substituted by K atoms or La atoms, respectively. The substitution of one Sr atom in the supercell corresponds to a charge-doping concentration of 12.5%, and that of two Sr atoms in different Sr layers to 25%. The lattice constants were fixed at the experimental values ($a = b = 9.5206$ Å and $2c = 2 \times 6.2002 = 12.4004$ Å) [25]. The Brillouin zone was sampled with a $7 \times 7 \times 6$ Monkhorst–Pack *k*-point mesh. All internal atomic positions were optimized until the forces on atoms reached a convergence criterion 0.01 eV/Å. In addition, we double checked the results by employing the virtual crystal approximation (VCA) to simulate various charge doping concentrations in $(Sr_{1-x},A_x)_2MnGe_2S_6O$ (A=K, La). The VCA corresponds to a weighted average of the potentials for Sr and K (La) atoms. The correlation effect in the 3*d* orbitals of Mn atoms was checked in the GGA+U framework by using the simplified rotationally invariant version of Dudarev et al. (effective *U*) [32].

3. Results and analysis

In the melilite-type oxysulfide $Sr_2MnGe_2S_6O$, the different layers formed by corner sharing MnS_4 and GeS_3O tetrahedra are separated by Sr atoms, while the Mn atoms in the same layer form a square lattice (Fig. 1c). Previous experiments determined that the magnetic ground states of $Sr_2MnGe_2S_6O$ and the isostructural $Sr_2MnGe_2O_7$ are in an intra-layer checkerboard AFM Néel order with a very weak inter-layer AFM coupling [24,25]. For the doped compound $(Sr_{1-x},A_x)_2MnGe_2S_6O$ (A = K, La), we thus mainly considered two typical magnetic orders: the same checkerboard AFM Néel order as the one in its parent compound as well as an FM order with both intra-layer and inter-layer ferromagnetic ordering. Moreover, our calculations demonstrate that the inter-layer magnetic coupling in $(Sr_{1-x},A_x)_2MnGe_2S_6O$ is also very weak compared with the intra-layer one, suggesting its two dimensional magnetic characteristics.

Fig. 2 shows the energy difference between the FM and AFM orders of the compound $(Sr_{1-x},A_x)_2MnGe_2S_6O$ as a function of charge doping concentration *x*. At zero charge doping, the magnetic ground state of $Sr_2MnGe_2S_6O$ is in the AFM order, which is in accordance with the experimental measurement [25]. With one K (La) atom substituting one Sr atom, equivalent to introducing 12.5% holes (electrons) into the compound, the FM order is energetically

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