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Strong ferromagnetism of two-dimensional δ–(Zn,Cr)S with shape deformation in both PBE and LDA + U calculations

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ABSTRACT

With density functional calculations, the enhancement of magnetic exchange energy (MEE) of two-dimensional (2-d) diluted magnetic semiconductor (DMS) δ–(Zn,Cr)S with shape deformation was investigated. The increase of lattice parameter *c* (perpendicular to the Cr layer) and decrease of *a* (parallel to the Cr layer) had a significant effect on the increase of MEE. Both PBE and LDA + U methods could enhance the MEE to a significant extent, which makes it superior to other δ-DMS found in initial research. The main mechanism by which increase the MEE is to vary the hole-states across the Fermi level with shape deformation, based on Zener's double exchange (DE) mechanism. This enriches the research into 2-d FM materials, which are candidates for next-generation electronic and optoelectronic applications.

1. Introduction

ZnS has a wide energy band gap (3.68 eV) and large binding energy (40 meV). Cr is a promising transition element dopant, for both optical and magnetic purposes, to form a diluted magnetic semiconductor (DMS) ZnCrS [1–3]. In particular, ZnCrS has attracted much interest and been employed extensively in diverse applications using nanoparticles in recent years [4–11]. The weak room temperature ferromagnetism is notable in ZnCrS nanoparticles with Cr doping at up to 20% by mass [7–11]; however, the mechanism underpinning the ferromagnetism thereof remains unclear. Before the research into ZnCrS particles had been developed, the mechanism of Cr in bulk ZnCrS had not been studied yet. Given the wide-gap of ZnS, some of the impurity states of Cr atoms falls within the gap [12]. It should be a *p*-type characteristic with a falling Fermi level within the impurity states in the gap, which makes ZnCrS ferromagnetic (FM) based on Zener double exchange (DE) [13–16]; however, this has not been discussed in detail at time of writing. To produce a high Cr doping concentration in bulk, the δ-doping, in which one layer of Zn atoms are substituted by Cr atoms in ZnS (named δ-ZnCrS) is used: this is a typical 2-d DMS and represents a promising material for future electronic and optoelectronic applications [17,18]. The effect of epitaxial strain on the magnetic properties of different materials have been studied elsewhere [19–23] using density functional theory (DFT) to increase the ferromagnetism. In this study, our focus is also on elucidating the enhancement of ferromagnetism and the mechanism of δ-ZnCrS by shape deformation.

2. Method and computational details

The Vienna *ab initio* simulation package (VASP) is used with the pseudo-potential plane wave method based on density functional theory (DFT) [24]. The electron-core interactions are described by using the projector-augmented wave (PAW) method to generate pseudo-potentials. The exchange correlations between electrons are of semi-local Perdew-Burke-Ernzerhof (PBE) form [25].

A cut-off energy (E_{cut}) of 365 eV was used to expand the plane wave functions. More results with E_{cut} values (365 eV, 415 eV, and 465 eV) prove that the Cr-Cr exchange interaction, which is defined by: $\Delta E_{AFM\text{-}FM} = E_{AFM} - E_{FM}$, converges to less than 2 meV. The Monckhorst-Pack scheme was used for 8 × 8 × 2*k*-point grids. For static calculations, the *k*-point grids measured 16 × 16 × 4. All atoms in the supercell were relaxed until the Hellmann-Feynman force was less than 10^{-2} eV/Å.

The crystal constant was found to be 5.45 Å. Four ZnS cubic cells are arranged along the *z*-direction (Fig. 1). A Cr plane substitutes for one of the Zn planes with periodic boundary conditions. As shown in Fig. 1, superlattice $CrS_1/ZnS_7$is formed as δ-(Zn,Cr)S, where a CrS zincblende

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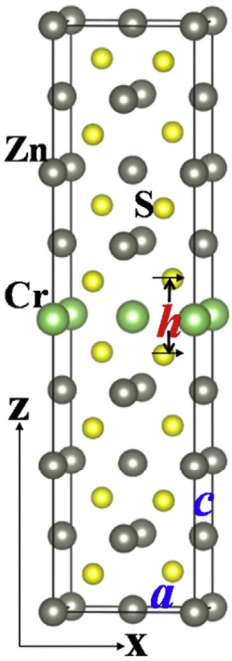

Fig. 1. Supercell for CrS_1/ZnS_7 configurations in ball-stick format. Middle grey and small yellow balls represent Zn and S atoms, respectively. Large light green balls represent Cr atoms: x and z are axes of the supercell, the y-axis is perpendicular to the xz-plane and is the same as the x-axis (not shown); a and c are the lengths of one crystal cell in the x- and z-directions respectively, denoted as lattice parameter. h is the layer heights. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

(ZB) monolayer is separated by a 5.45 Å × 4 Å ZnS layer and the Cr concentration x is 0.125. This supercell is large enough to consider all modes of shape deformation. Besides, the CrS_1/ZnS_{15} structure with $x = 0.0625$ is also used to describe the magnetic properties with shape deformation. δ-(Zn,Cr)S cells can vary with changes to two parameters: c and a, as shown in Fig. 1. For example, for CrS_1/ZnS_7, when the lattice parameter c or a varies, the length of the supercell in the z-direction becomes $4c$, and that in the x- and y-directions are both a, while for CrS_1/ZnS_{15}it is $8c$ in the z-direction. Here, c and a vary independently to simulate all kinds of shape deformation.

3. Results and discussion

3.1. Exchange energy enhanced by shape deformation

The values of c and a were set around the ZnS crystal constant 5.45 Å, ranging from 5.25 Å to 5.65 Å in increments of 0.05 Å. The magnetic exchange energy (MEE) for each configuration is $E_{AFM\text{-}FM}$. The MEE of CrS_1/ZnS_7 and CrS_1/ZnS_{15} with shape deformations are shown in Figs. 2 and 3, respectively, where the abscissa represents the variation of c and the ordinate represents the variation of a. Each horizontal line parallel to the abscissa axis is fixed at a certain value of a, while c varies from 5.25 Å to 5.65 Å in increments of 0.05 Å. Similarly, the vertical line parallel to the ordinate axis is fixed at a certain value of c, while a varies from 5.25 Å to 5.65 Å in increments of 0.05 Å. The crossing points of horizontal and vertical lines are the calculated values. The left-hand panels of Fig. 2 are FM energy contours, while the right shows MEE contours plotted for each configuration. The black diagonal in MEE panels indicates a special deformation process, in which the volume $V = 4 \times c \times a^2$ of the supercell is kept constant during shape deformation.

As shown in Fig. 2(a) and (c), it is clear that the FM energy varies slowly with c, while does so rapidly with a. Comparing Fig. 2(a) and (c),

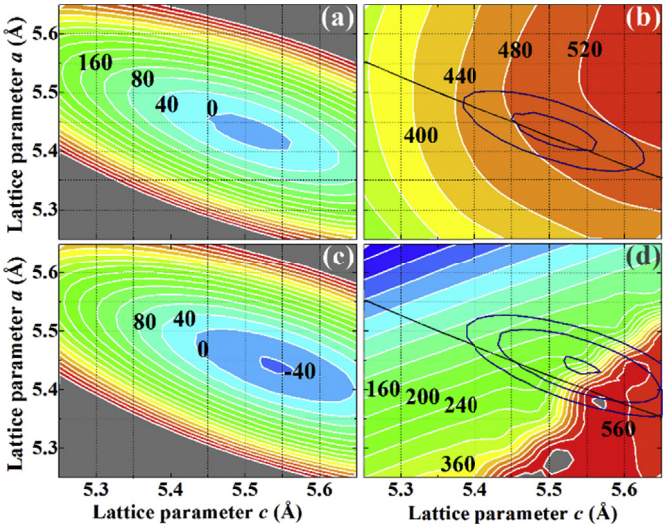

Fig. 2. (a) and (b) are the FM energy and exchange energy contours of CrS_1/ZnS_7 with the shape deformation of lattice parameter a and c, respectively. Contour values are labeled in the figures. The black line in (b) indicates the shape deformation where the volume of the supercell equals to the initial one. The circles in (b) are the contour lines in (a). (c) and (d) are the same as (a) and (b) respectively, but with U.

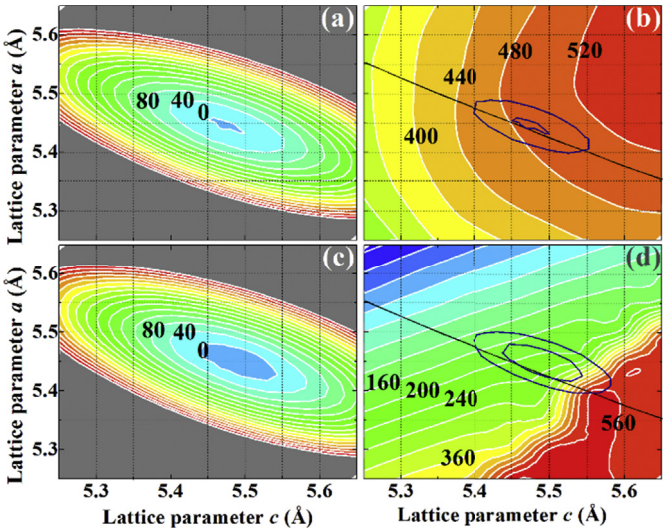

Fig. 3. Similar to Fig. 2, but for CrS_1/ZnS_{15}.

it can be found that the variation of FM energy in the LDA + U method is a little slower than that under the PBE method: however, MEE changes very fast with c while does so slowly with a, as shown in Fig. 2(b). At the same volume V, the variation of MEE is also significant. In Fig. 2(d), MEE variation is obvious with both a and c, but greater with a in the LDA + U method. MEE changes quasi-linearly with a or c (upper left corner, Fig. 2(d)). Comparing Fig. 2(b) and (d), it can be found that the variation of MEE in the LDA + U method is greater than that when using the PBE method.

MEE is 480 meV with no deformation in the PBE method. In the zone where $c > 5.45$ Å and $a > 5.45$ Å, most kinds of shape deformation can enhance the MEE and make it exceed 480 meV. The possibility of shape deformation is shown by the FM energy in Fig. 2(a), where the FM energy of the initial supercell is set to zero and the other FM energy with shape deformation corresponds to the initial state. Too large an FM energy makes the shape deformation process difficult in experimental terms, so only those structures with an FM energy of less than 40 meV should be considered. Below 40 meV, there are only a few points with a