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The electronic, magnetic and optical properties of Co doped marcasite FeS_2

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ABSTRACT

The electronic, magnetic and optical properties of Co doped marcasite FeS_2 compounds have been investigated through the first-principles calculations. No imaginary frequency emerges in the phonon dispersion curves confirms the Fe_7CoS_{16} and $Fe_6Co_2S_{16}$ compounds are dynamical stable. Although the pure Fe_8S_{16} compound is a nonmagnetic semiconductor with band gap of 1.17 eV, the Fe_7CoS_{16} compound changes to a magnetic semiconductor with a very narrow band gap of 0.106 eV, the $Fe_6Co_2S_{16}$ compound changes to a half-metal with half-metal band gap of 0.37 eV in spin-down channel. For all three considered configurations of the $Fe_6Co_2S_{16}$ compound, the ferromagnetic state is preferred over antiferromagnetic state, especially for smaller separation distance of two doped Co atoms. The higher Curie temperatures than room temperature indicates the $Fe_6Co_2S_{16}$ compound is a promising candidate for spintronics applications. In addition, the calculated optical properties shows that Fe_7CoS_{16} and $Fe_6Co_2S_{16}$ compounds have stronger absorption than Fe_8S_{16} compound when the wavelength more than 500 nm, which suggests the compounds are potential candidates for solar cells.

1. Introduction

Iron disulfide (FeS_2) has been researched extensively in many respects. It can be used as photovoltaic materials [1], anode material for lithium ion batteries [2], counter electrode materials for dye-sensitized solar cells [3], thermo-electric materials [4], spintronics [5] and so on. FeS_2 possesses glorious electron mobility [6], large photon absorption coefficient of $10^5\ cm^{-1}$ and it is made up of natural abundant and environmental friendly elements [7–10]. There are two polymorphs for FeS_2 in naturally: pyrite FeS_2 (p-FeS_2) and marcasite FeS_2 (m-FeS_2). The structure of p-FeS_2 belongs to space group $Pa\bar{3}$ in cubic crystal system, while m-FeS_2 possesses orthorhombic crystal system in space group *Pnnm*. Very earlier research have provided band gap of 0.34 eV for m-FeS_2 [11], so that it always be considered as a non-convenient impurity of p-FeS_2 in photovoltaic materials. Recent published studies have predicted that m-FeS_2 have a band gap quite similar to that of p-FeS_2 [12–14], which made researchers began to study m-FeS_2 seriously. L. F. Wu and coworkers [15] reported the advantageous role of m-FeS_2 in photo-electrochemical applications of iron sulfide-based materials. Their research indicated that the FeS_2 films mixed pyrite-marcasite phase not only improve photo-currents and photo-response considerably, but also increase the stability of the films against photo-corrosion and reduce the dark current prominently. T. T. Li et al. [16] synthesized the marcasite FeS_2 nanoparticles for the first time in colloidal solution via a hot-injection protocol. Their research indicated that compared with p-FeS_2 and other iron sulfides, the m-FeS_2 exhibit more excellent lithium ion storage and more stable charge-discharge performance as the anode materials in lithium ion battery application. D. G. Moon et al. [17] investigated the influence of marcasite on iron pyrite thin films, they found that marcasite should have a band gap of approximately 0.85–0.88 eV with a higher absorption coefficient than pyrite, and the pyrite/marcasite film have a larger photocurrent density than pure pyrite. The pioneer's works clearly suggested that m-FeS_2 should be a useful semiconductor in photovoltaic materials.

It is a universal approach that introducing the impurities into a material artificially to tune the electronic, magnetic and optical properties of the material. Semiconductors doped with magnetic impurities are called Diluted magnetic semiconductors (DMSs) [18]. DMSs have attracted extensive attention in recent years due to their potential applications as a new type of functional materials. It can be used in magnetic sensors, spin-polarized light-emitting diode and so on. Those kinds of materials continue to challenge our understanding. The purpose of the research is to find DMSs with high Curie temperature for the applications of spintronic devices. Room-temperature ferromagnetism has been reported in Mn-doped $CdGeP_2$ [19], Co-doped anatase TiO_2 [20], Co-doped rutile TiO_2 [21], V-doped rutile TiO_2 [22] and so on. To the best of our knowledge, the electronic, magnetic and optical properties of Co doped m-FeS_2 have not been reported in detail so far. In present work, we investigate the electronic, magnetic and optical properties of m-FeS_2 and Co doped m-FeS_2 compounds. The calculation

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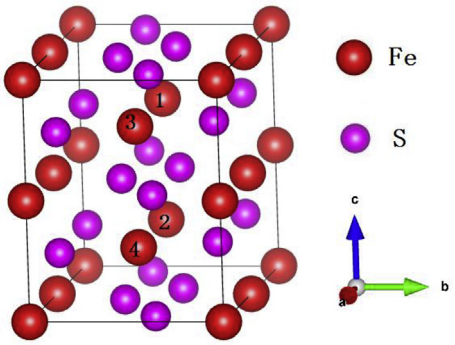

Fig. 1. The 2 × 1 × 2 supercell of marcasite FeS_2. Red and pink ball represent Fe and S atoms, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

details are given in section 2, the results and discussions are shown in section 3. Finally, the summary and conclusions are given in section 4.

2. Computational details

First-principles calculations are performed with the Vienna ab-initio simulation package (VASP) [23–26] based on pseudo-potential plane wave method within the frame work of the density function theory (DFT). The projector augmented wave (PAW) potentials [27] are used to describe the electron-ion interactions. The exchange and correlation terms are described with the generalized gradient approximations (GGA) [28] of Perdew-Burke-Eruzerh (PBE) formulation, as well as taking into account on-site coulomb repulsive interaction (GGA + U) [29–31], an effective U value of 2.5 eV for Co-d orbital [32] and 2 eV for Fe-d orbital [14]. In the structure calculation, a plane-wave basis set with energy cut off of 500 eV is used. For the Brillouin-zone sampling,

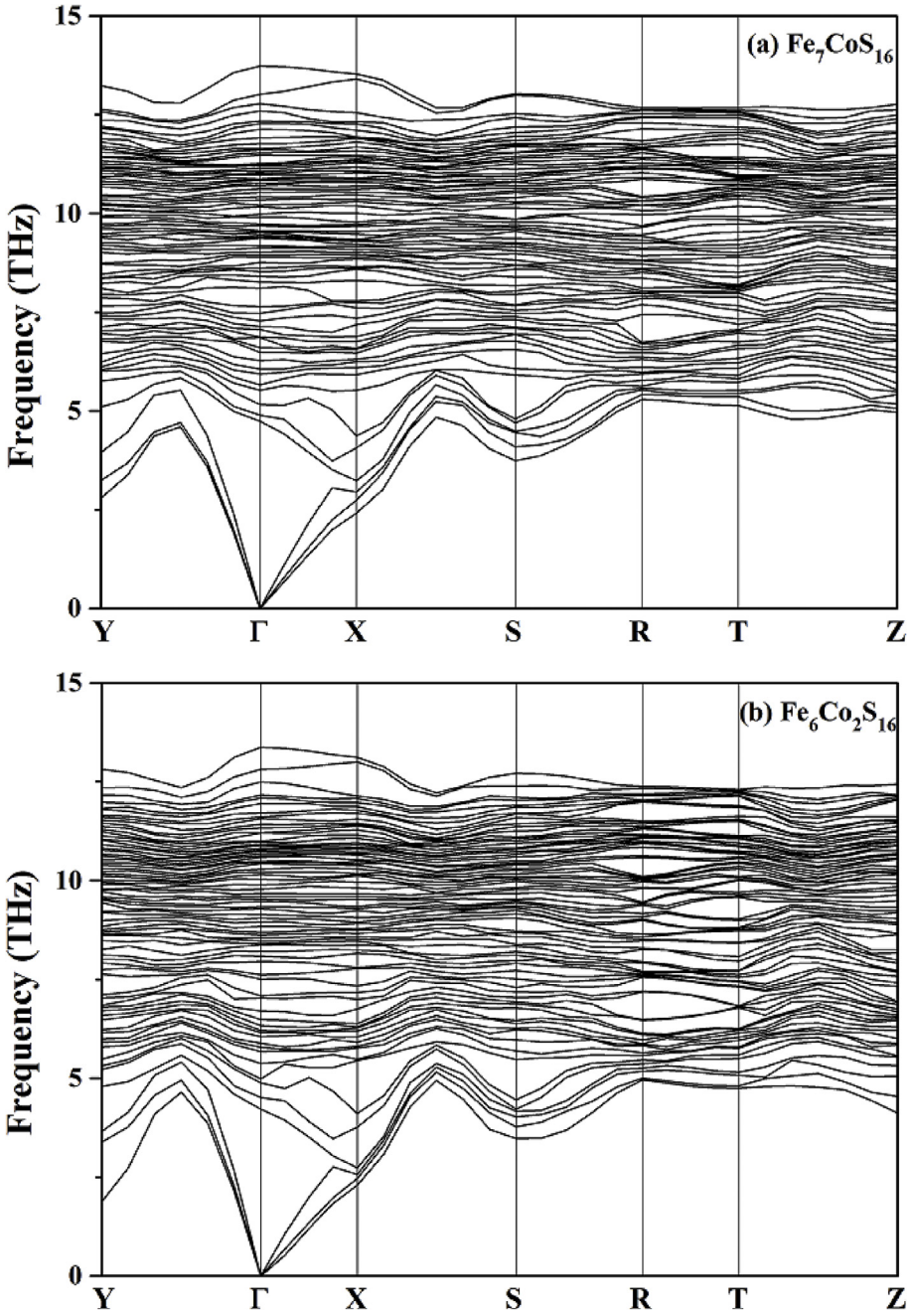

Fig. 2. Phonon dispersion curves of (a) Fe_7CoS_{16} compound, (b) $Fe_6Co_2S_{16}$ compound.