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Strain effects on electronic structures of monolayer iron sulphide and selenide

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ABSTRACT

Structural and electronic properties of single atomic layers of FeS and FeSe superconductors have been investigated from first principles within the density functional theory (DFT). For both systems the mixed single-stripe and block-checkerboard type antiferromagnetic ground states are predicted. Namely, the single-stripe and block-checkerboard orders are almost degenerate. The metal-insulator transition in a hypothetical block-checkerboard phase of FeS occurs only under significant tensile strain, i.e. for in-plane lattice parameters larger than 3.8 Å. Compressive strain leads to almost a complete disappearance of magnetism in FeS system, whereas tensile strain strengthens it. The electronic structure of FeS monolayer in nonmagnetic phase is similar to that of FeSe, exhibiting the (π, π) nesting between hole- and electron-like Fermi surface sheets. The findings presented here explain different characters of superconductivity in FeS and FeSe materials and encourage further experimental studies on FeS-based thin films and heterostructures.

1. Introduction

The recent discovery of superconductivity (SC) in the PbO-type FeS [1] has initiated numerous studies of this system as another member of a rich family of iron chalcogenide superconductors [2,3]. The superconducting critical temperatures (T_c) of 4–5 K [1,4–9] reported for FeS are lower than that of the FeSe superconductor (T_c = 8 K) [10]. Furthermore, SC in the sulphur based compound is suppressed by pressure [8,9] in contrast to the selenide that exhibits a rapid increase of T_c under pressure [11,12]. A multiband character [13] of a strongly coupled [14] superconducting state in FeS was revealed. Furthermore, a coexistence of low-moment disordered magnetism and SC with the fully gapped order parameter, which is satisfactorily described by a two-gap *s*-wave model [8], was reported, although some studies suggested a nodal SC gap [5,6] in this system. Meantime, a plain s-wave gap was revealed in recent experimental studies on FeSe monolayer [15], whereas in the bulk FeSe material anisotropy of the SC gap was found [16]. One may expect that the nature of SC mechanism in FeS is similar to that of FeSe, i.e., unconventional pairing driven by some magnetic fluctuations [17,18].

Magnetic interactions in FeSe, being different from those of most pnictides, demonstrate an unusual and unanticipated frustration, which suppresses magnetic order and triggers ferro-orbital order in the nematic phase [19]. This fact may explain the non-monotonic pressure dependence of the superconducting critical temperature in FeSe. A strong cooperative coupling of pressure-induced magnetic order and nematicity was recently reported for this system [20]. Furthermore, the stabilization of the block-checkerboard phase in Fe-based superconductors is connected with the third-neighbor interactions [21,22].

The theoretical DFT-based investigations indicated that the electronic structure of bulk FeS is very similar to that of FeSe superconductor [23–25]. Namely, the Fermi surface (FS) of FeS consists of two hole- and two electron-like FS cylinders at the Brillouin zone center and corner, respectively. The experimental studies of the Shubnikov-de Haas and de Haas-van Alphen oscillations confirmed existence of quasi-two-dimensional FS cylinders in FeS [26]. It is worth noting that the band renormalization in iron chalcogenides, discussed based on the photoemission data [2,3], concerns not only a size of particular features of band structure, but may also be strongly orbital dependent [27]. Furthermore, the electronic structure of FeSe supports the possible existence of the Fulde-Ferrell-Larkin-Ovchinnikov superconducting phase [28].

Recent experiments performed on single-layer FeSe films grown on $SrTiO_3$ have shown that interface effects can lead to a significant

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enhancement of SC (T_c above 100 K) in such heterostructures [29,30]. Although their electronic structures are somewhat different from that of the bulk FeSe material [22,31–34], investigations of two-dimensional, single-layer iron chalcogenides [22,35,36] remain an interesting area of research for further inferring an interplay between the unconventional SC and magnetism in Fe-based systems.

In this work, the structural, electronic and magnetic properties of a single FeS layer, compared with those of the FeSe counterpart, are investigated by *ab initio* calculations. The discussion of a correspondence between the electronic structures of bulk and monolayer FeS systems is carried out. The findings presented here may be useful for better understanding magnetism and SC in the FeS material. Particularly, the selection of substrates for FeS-based heterostructures is a critical issue for further experimental undertakings.

2. Computational methods

Band structure calculations for monolayer FeS and FeSe systems have been performed in the framework of DFT, i.e., with the full potential local-orbital (FPLO-9) package [37]. Valence-basis sets were automatically selected by the internal procedure of FPLO-9. The $12 \times 12 \times 1$ **k**-point grids were employed. The total energy convergence of 1.0×10^{-8} Ha and the tolerance of the maximal force of 1.0×10^{-3} eV/Å were used.

The GGA-PBE [38] parameterization of the exchange-correlation functional was selected. Despite the fact that this approach yields a strongly overestimated interlayer distance in the bulk FeSe compound [39,40], it better describes the in-plane lattice parameters than the LDA functional [41] and the investigations with the van der Waals correction (DFT-D2) included [39]. One may expect that in the case of a single atomic layer the van der Waals interaction may be less significant than in the case of a bulk material. This assumption is examined and discussed in the further text, based on the results reported in the GGA DFT-D2 study of a FeSe monolayer [35].

The nonmagnetic (NS) and checkerboard (AFM1) phases of FeS and FeSe single layers were simulated with the tetragonal supercells of the PbO-type, whereas the $(\sqrt{2}a \times \sqrt{2}a \times c)$, $(2a \times a \times c)$, and $(2\sqrt{2}a \times \sqrt{2}a \times c)$ supercells were employed for single- (AFM2), double-stripe (AFM3), and block-checkerboard (AFM4) antiferromagnetic orders, respectively, as depicted in Fig. 1. Such monolayers were separated with vacuum region of 12 Å. The strain in *ab*-plane was simulated for an arbitrary set of lattice parameters a via the optimization of the free chalcogen atom positions (z_{ch}) in the unit cell (u.c.) due to forces. Although the possible nontetragonal distortions of u.c. were neglected, this approach is adequate for discussion of properties of systems deposited on cubic or tetragonal substrates. It is worth noting that the recent study [35] suggested that monolayer systems of iron chalcogenides have large enough mechanical flexibility to support critical strains higher than 30 %. Equilibrium lattice parameters were derived from the fit of a cubic polynomial to $E(a)$ dependence. The calculated values of the magnetic stabilization energy are given in relation to the nonmagnetic phase.

3. Results and discussion

The total energy as a function of a lattice parameter a of the FeS monolayer, calculated for nonmagnetic and magnetically ordered u.c. (see Fig. 1), is presented in Fig. 2(a). Only the AFM1 (single-stripe) magnetic order is slightly favorable for $a < 3.65$ Å, because its total energy is almost equal to that of the NS phase. Other AFM states emerge for lattice parameters larger than 3.65 Å.

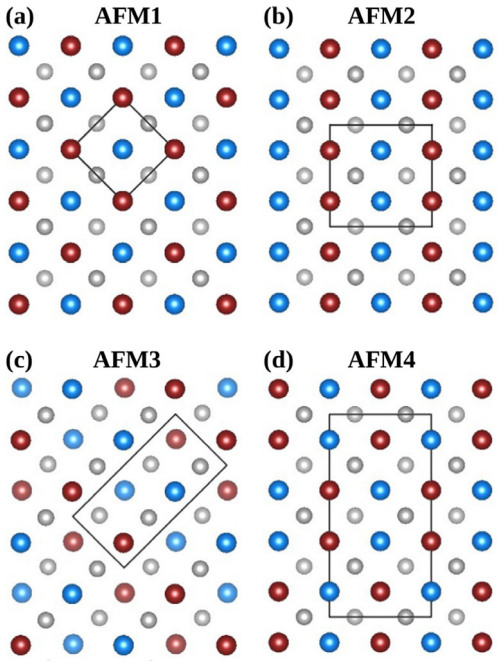

Fig. 1. A top view of the checkerboard (a, AFM1), single-stripe (b, AFM2), double-stripe (c, AFM3), and block-checkerboard (d, AFM4) spin arrangements in monolayer FeS. Iron atoms with spin up/down are presented with red/blue balls, whereas sulphur atoms are smaller grey balls. The borders of particular magnetic unit cells are marked with a solid line. Depicted with the VESTA package [64]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

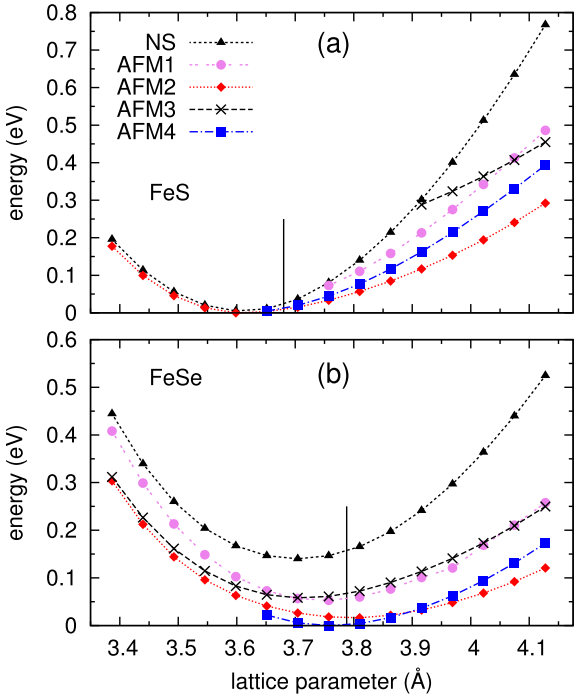

Fig. 2. The total energy per formula unit calculated for FeS (a) and FeSe (b) for nonmagnetic and various antiferromagnetic orders (see Fig. 1). Experimental lattice parameters of bulk systems [1,42] are marked with vertical lines.

Although experimental studies suggest that the magnetic ordering in the bulk FeSe is unstable in equilibrium [20], the magnetic arrangement in our DFT-derived results for the FeSe monolayer is quite robust. As depicted in Fig. 2(b), all magnetic phases are