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Strain Control of the Tunable Physical Nature of a Newly Designed Quaternary Spintronic Heusler Compound ScFeRhP

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Abstract: Recently, an increasing number of rare-earth-based equiatomic quaternary compounds have been reported as promising novel spintronic materials. The rare-earth-based equiatomic quaternary compounds can be magnetic semiconductors (MSs), spin-gapless semiconductors (SGSs), and half-metals (HMs). Using first-principle calculations, we investigated the crystal structure, density of states, band structure, and magnetic properties of a new rare-earth-based equiatomic quaternary Heusler (EQH) compound, ScFeRhP. The results demonstrated that ScFeRhP is a HM at its equilibrium lattice constant, with a total magnetic moment per unit cell of 1 μ_B . Furthermore, upon introduction of a uniform strain, the physical state of this compound changes with the following transitions: non-magnetic-semiconductor-(NMS) \rightarrow MS \rightarrow SGS \rightarrow HM \rightarrow metal. We believe that these results will inspire further studies on other rare-earth-based EQH compounds for spintronic applications.

Keywords: quaternary Heusler compound; first-principle calculations; physical nature

1. Introduction

Since the first report on half-metal (HM) by Groot et al. [1], various Heusler compounds have been verified by theoretical approaches and experiments to be HM materials. The HM Heusler alloys attract significant interest owing to their novel physical properties [2–6].

Typically, Heusler-based HMs can be divided into three types: half-Heusler HMs [3], full-Heusler HMs [4], and quaternary Heusler HMs [5]. The quaternary Heusler alloys (XMYZ) can be regarded as a combination of two full-Heusler alloys: X_2YZ and M_2YZ (X, Y, M are individual 3d or 4d transition elements, while Z is an atom of the main group). Many quaternary Heusler HMs have been investigated by first-principle approaches. For example, Han et al. [6] have investigated a novel equiatomic quaternary Heusler (EQH) alloy YRhTiGe, concluding that it is an HM with a ferromagnetic ground state. Moreover, they studied its mechanical anisotropy, as well as dependence on the direction of shear modulus and Young's modulus in detail. New quaternary HMs, FeRuCrP and FeRhCrP [5], have been studied by Ma et al. in 2017; strain has been introduced to investigate its effect on the HM states.

In recent years, Wang [7] has theoretically predicted a novel type of materials, referred to as spin-gapless semiconductors (SGSs). The SGSs can be categorized as new members of the zero-gapless material family. Following this study, many Heusler-based SGSs [8] were studied. Recently, Zhang et al. studied the LuCoCrGe EQH compound [9], revealing that it is a highly dispersive gapless HM under strain.

Figure 1 illustrates a HM, SGS, and magnetic semiconductor (MS). Figure 1a shows that one of the channels (spin-down (minority) channel) is metallic, while the other one (spin-up (majority) channel)

exhibits a semiconducting behavior. Figure 1b shows that there is a band gap for the spin-up channel between the two bands (conduction and valence bands). The behavior is different for the spin-down channel, exhibiting a zero-gap between these bands; this behavior corresponds to SGS. In Figure 1c, two semiconductor-type band gaps are observed in both channels, corresponding to MS properties.

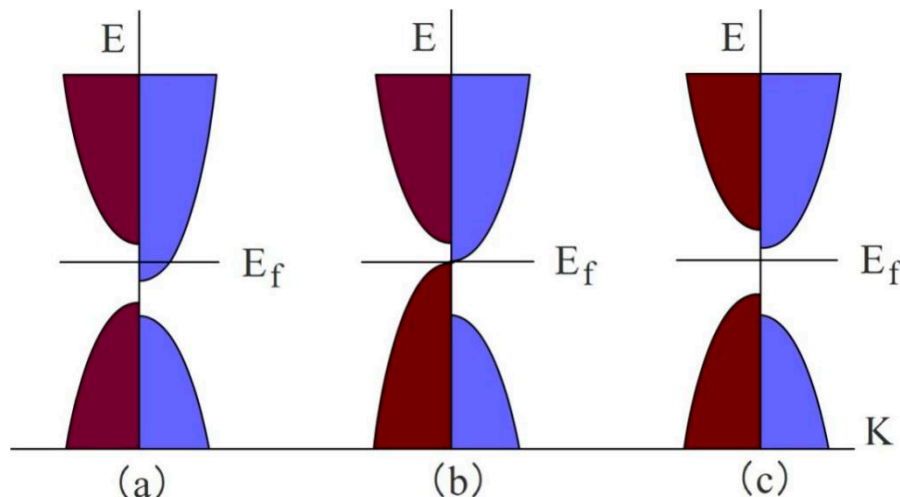


Figure 1. Schematics of the densities of states of a (a) half-metal (HM), (b) spin-gapless semiconductor (SGS), and (c) magnetic semiconductor (MS).

In this study, we employed first-principle calculations to investigate the crystal structure, electronic structure, and magnetic properties of a new rare-earth-containing EQH compound ScFeRhP. We demonstrate that this compound is HM at its equilibrium lattice constant. Rare physical transitions with an SGS feature can be observed at different strain magnitudes.

2. Calculation Method

We calculated the band structure and magnetic properties of ScFeRhP by the plane-wave pseudopotential method [10,11], using the Cambridge Serial Total-Energy Package (CASTEP) software. We studied the interaction between the valence electrons and nuclei by the method of ultra-soft pseudopotentials [12]. The generalized gradient approximation (GGA) was used to calculate the exchange and correlation between electrons [13] using the scheme of Perdew-Burke-Ernzerhof (PBE) [14]. In all calculations, a k -point mesh of $12 \times 12 \times 12$ and plane-wave basis-set cut-off of 450 eV were used. The above parameter settings ensure accuracy of the calculation results.

3. Results and Discussion

3.1. Structural Stability and Total Energy

In general, the EQH compounds have LiMgPdSn-type structures [15]. Three types of crystal structures and their distinct atomic positions of the ScFeRhP EQH compound are shown in Figure 2 and Table 1, respectively. Following the atom-occupation rule, Rh tends to occupy the site D ($3/4, 3/4, 3/4$), P and Sc tend to occupy the A ($0, 0, 0$) and C ($1/2, 1/2, 1/2$) sites, respectively, and Fe tends to occupy the B ($1/4, 1/4, 1/4$) site. Therefore, for the ScFeRhP compound, type I (see Figure 2) is the most probable configuration owing to its lowest energy.

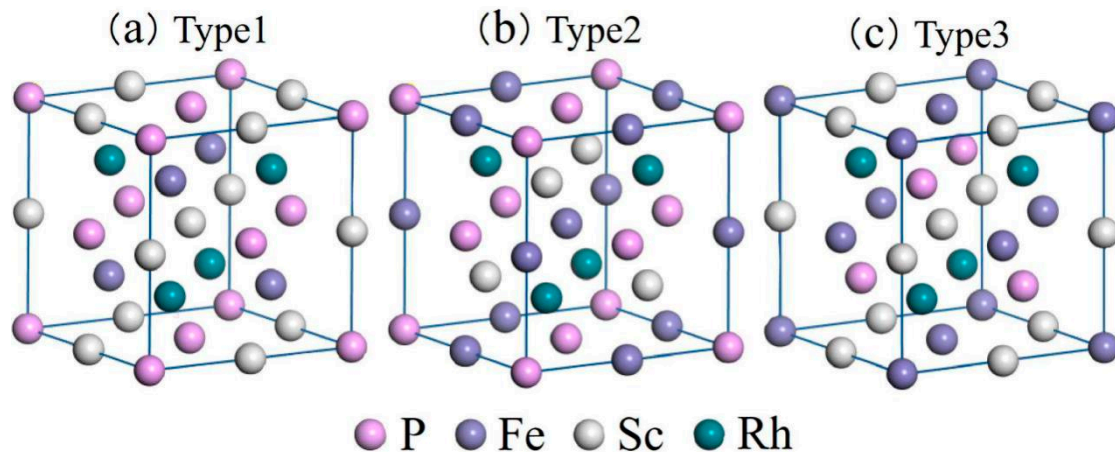


Figure 2. Three possible crystal structures (a) type 1, (b) type 2, (c) type 3 for ScFeRhP compound.

Table 1. Three crystal-structure atomic positions of the ScFeRhP equiatomic quaternary Heusler (EQH) compound.

Type	P	Fe	Sc	Rh
Type 1	A (0, 0, 0)	B (1/4, 1/4, 1/4)	C (1/2, 1/2, 1/2)	D (3/4, 3/4, 3/4)
Type 2	A (0, 0, 0)	C (1/2, 1/2, 1/2)	B (1/4, 1/4, 1/4)	D (3/4, 3/4, 3/4)
Type 3	B (1/4, 1/4, 1/4)	A (0, 0, 0)	C (1/2, 1/2, 1/2)	D (3/4, 3/4, 3/4)

For geometric optimization of the ScFeRhP EQH compound, the crystal cell energy is minimized as a function of the lattice constant. The three possible crystal structures are shown in Figure 2. Each of them has ferromagnetic (FM) and non-magnetic (NM) states. We calculated the energies by the CASTEP software. Figure 3a shows total energies in FM states for the type 1, 2, and 3 structures, respectively, and Figure 3b shows the energies of both FM state and NM state for type 1 structure. Among the considered cases the calculated result that the type 1 structure at the FM state exhibits the minimum energy. More details about the equilibrium lattice constants and the total energies of these three type structures can be seen in Table 2. This indicates that the most stable of these structures is the type 1 structure at the FM state. According to the calculations, the equilibrium lattice constant of the ScFeRhP EQH compound is 5.97 Å.

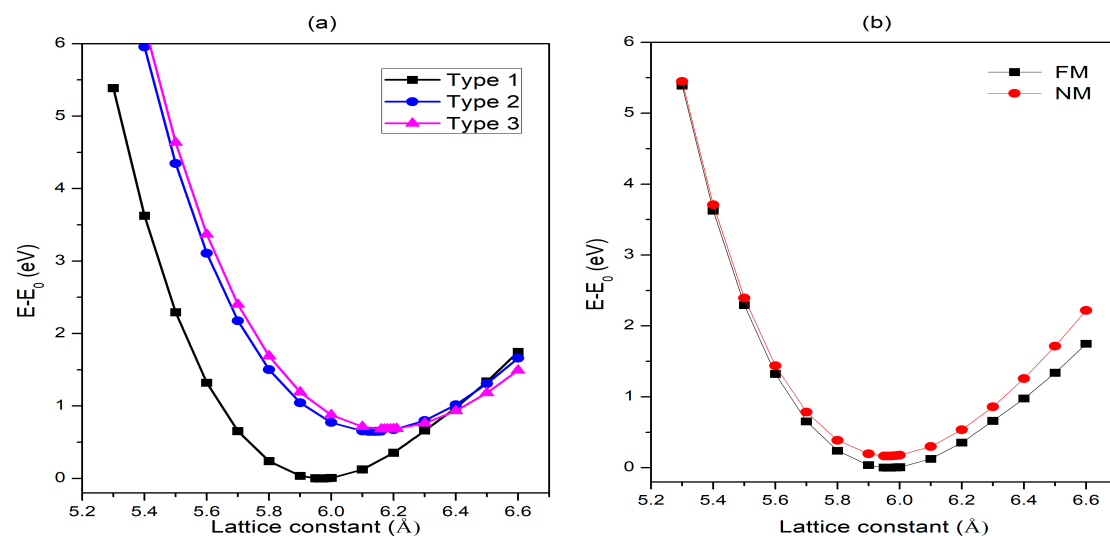


Figure 3. Total-energy-lattice-constant curves of the ScFeRhP compound in ferromagnetic (FM) states for the type (a) 1, 2, and 3 structures, and (b) FM and non-magnetic (NM) states for type 1.

Table 2. The equilibrium lattice constant and minimum total energy of each type for both FM and NM magnetic states.

States	Calculated Value	Type 1	Type 2	Type 3
FM	Equilibrium lattice constant	5.97 Å	6.14 Å	6.18 Å
	Total energy	−2931.40 eV	−2930.75 eV	−2930.72 eV
NM	Equilibrium lattice constant	5.96 Å	6.08 Å	6.10 Å
	Total energy	−2931.23 eV	−2929.80 eV	−2930.06 eV

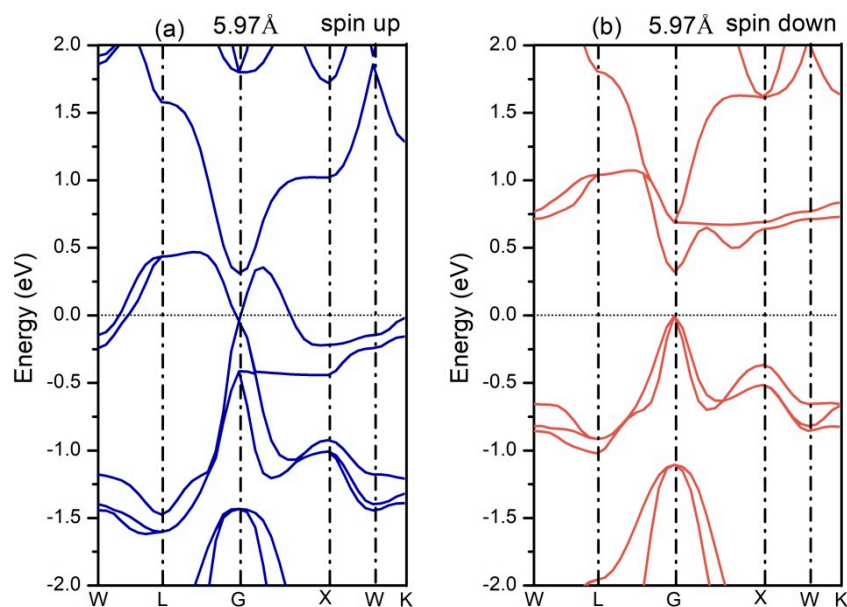
3.2. Electronic Structure and Slater–Pauling Rule

The partial and total (M_t) element magnetic moments, and total number of valence electrons (Z_t) of this compound at the most stable configuration are shown in Table 3. The M_t of the ScFeRhP EQH compound is 1 μ_B , while its total number of valence electrons is 25. This EQH compound obeys the Slater–Pauling rule: $M_t = Z_t - 24$ [16].

Table 3. Partial and total magnetic moments (μ_B), calculated equilibrium lattice constant, Z_t , and Slater–Pauling (S–P) rule for the ScFeRhP compound.

Compound	Total	P	Fe	Sc	Rh	a (Å)	Z_t	S–P Rule
ScFeRhP	1.00	0.04	0.98	−0.24	0.22	5.97	25	$M_t = Z_t - 24$

Figure 4 shows the calculated band structures for the ScFeRhP compound. The band structure reveals the half-metallicity of this compound near the Fermi level. The spin-up channel exhibits a metallic character, while the spin-down channel exhibits a semiconducting character. Therefore, based on the obtained band structures and magnetism, we can conclude that the ScFeRhP EQH compound is a HM.

**Figure 4.** Band structures of the (a) spin-up and (b) spin-down channels of the ScFeRhP EQH compound at its equilibrium lattice constant.

We analyze the origin of the band gap at the spin-down channel in Figure 5. According to the study of Galanakis et al., P has completely occupied 1s and 3p states. We need to consider only the hybridization character of the 3d and 4d states of the ScFeRhP EQH compound, as shown in Figure 5. For this alloy, the d_4 and d_5 orbits of the Fe and Sc atoms couple forming antibonding e_u and bonding e_g states. The d_1 , d_2 , and d_3 orbits of the Fe and Sc atoms couple forming antibonding t_{1u} and bonding

t_{2g} states. The same states of the Rh atom hybridize with the above orbits, yielding 15 orbits ($3 t_{2g}$, $2 e_g$, $2 e_u$, $3 t_{1u}$, $3 t_{2g}$, and $2 e_g$). There are 8 occupied orbits under the Fermi level (Figure 5). Combined with the $3p$ and $1s$ orbitals generated by P, there are a total of 12 orbits below the Fermi level; therefore, this compound follows the Slater-Pauling rule: $M_t = Z_t - 24$.

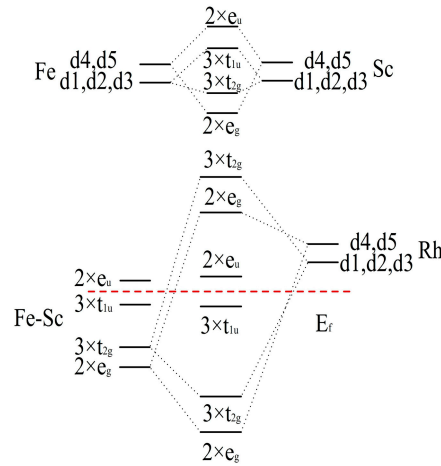


Figure 5. d -Orbit hybridization of the Rh ($4d$) and Fe/Sc ($3d$) transition elements in the ScFeRhP EQH compound.

In order to explain the origin of the band gap [17], we analyzed the partial densities of states (PDOS) and total density of states (TDOS) of ScFeRhP; the results are shown in Figure 6. The PDOS indicate that the TDOS at the Fermi level are mostly attributed to the Fe $3d$ and Rh $4d$ states. The PDOS of the P atoms and rare-earth element Sc are significantly lower near the Fermi level compared with those of the Fe and Rh atoms. Figure 6 reveals that the Fe element exhibits a stronger spin splitting at -1.4 eV in the majority channel and -0.8 eV in the other channel for the bonding state. For the Rh element, the bonding state was observed mostly in the range of -3.5 eV to -4 eV in the majority channel and in the range of -3 eV to -3.5 eV in the other channel.

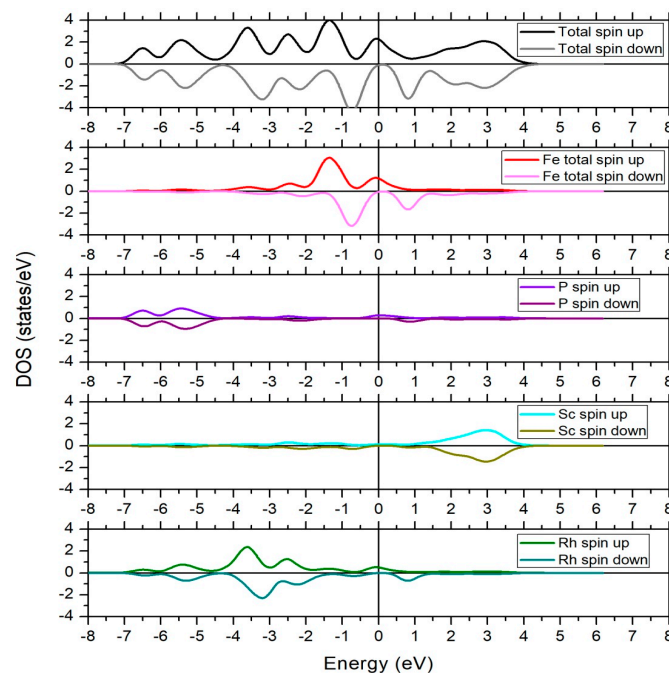


Figure 6. Total density of states (TDOS) and partial densities of states (PDOSs) for ScFeRhP.

3.3. Magnetic Properties

The magnetic behavior of the ScFeRhP alloy at strained lattice constants is discussed in detail in this section. The M_t of the ScFeRhP EQH compound is $1 \mu_B$ at its equilibrium lattice constant, and it remains almost unchanged when the lattice constant changed in a large range. The main contribution to the magnetic moment originates from the Fe atoms, as shown in Table 3. The M_t and partial magnetic moments at strained lattice constants of the ScFeRhP compound are presented in Figure 7. According to the actual conditions, we focus on compressive and expanded lattice constants in the range of 5.30 Å to 6.10 Å. As shown above, the total magnetic moment of the ScFeRhP EQH compound is $1 \mu_B$ at its equilibrium lattice constant. The magnetic moment decreases with the increase of the lattice constant for both P and Sc atoms; the magnetic moment of the Fe atom continuously increases, while that of the Rh atom is almost constant.

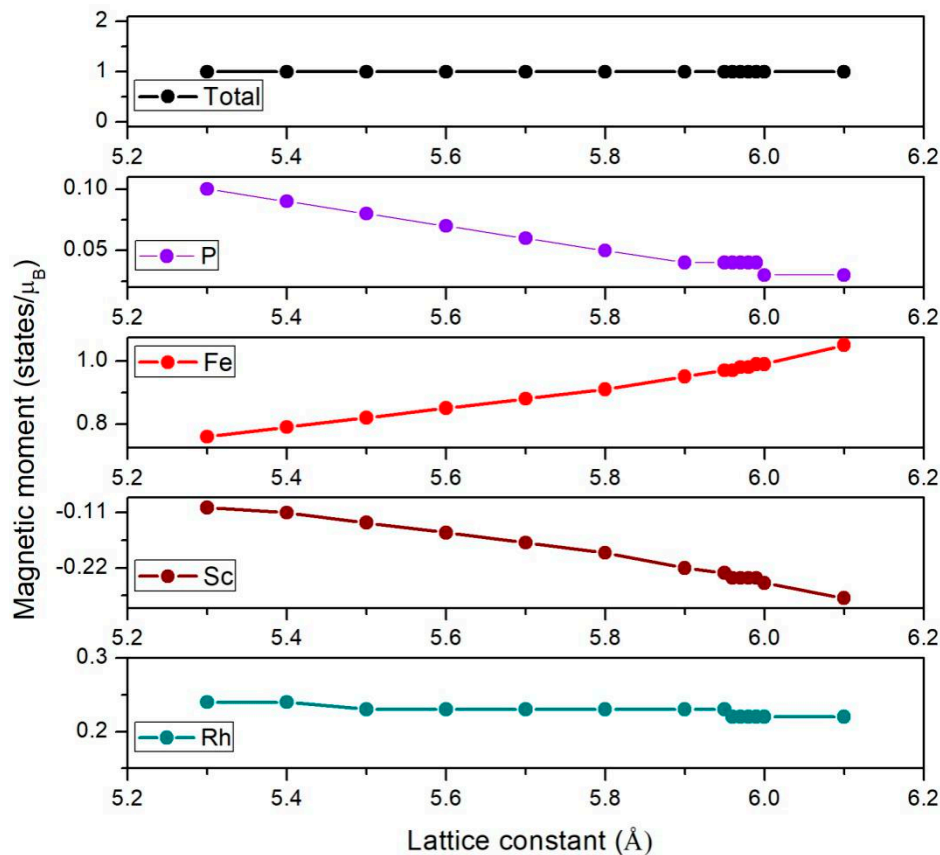


Figure 7. Partial and total magnetic moments as a function of the lattice constant of the ScFeRhP EQH compound.

3.4. Transitions of the Physical State under Uniform Strain

In this section, we discuss the change of the physical state of the compound under uniform strain. A novel distinct transition can be observed in the obtained band structure of the ScFeRhP compound at its strained lattice constants. The conversion of non-MS-(NMS)-to-MS-to-SGS-to-HM-to-M for this compound is shown in Figure 8.

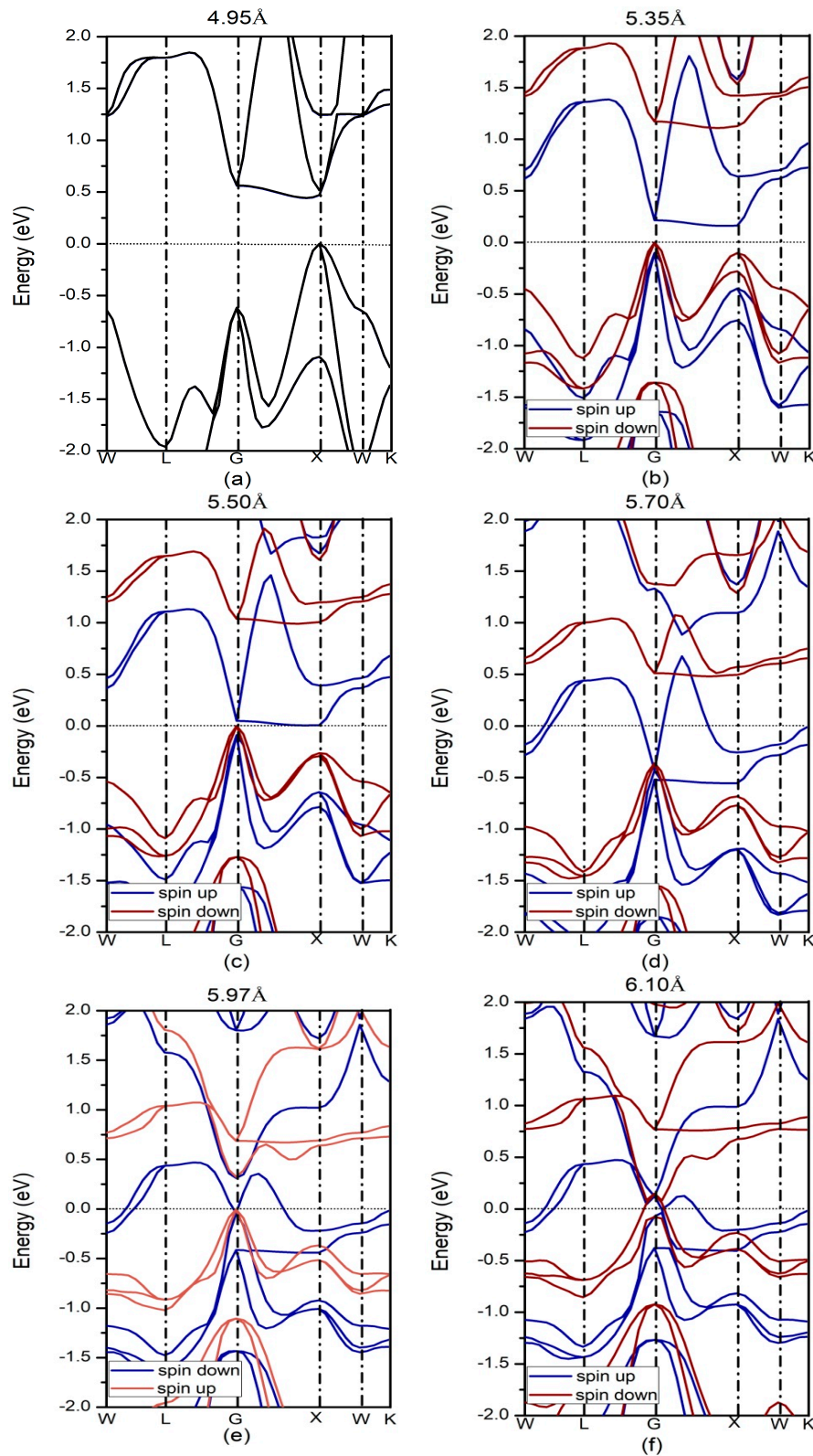


Figure 8. (a–f) are band structures under strained lattice constants of 4.95 Å, 5.35 Å, 5.50 Å, 5.70 Å, 5.97 Å, and 6.10 Å, respectively, for ScFeRhP compound.

The detailed band structures are plotted in Figure 8. With the increase of the lattice constant, the valence band moves down in the minority channel at the X-point, and moves up in the majority channel at the G-point, whereas in the conduction band, the opposite behavior is observed. If the

lattice constant is smaller than 4.95 Å, the compound is NMS. If the parameter is in the range of 4.95 Å to 5.495 Å, the compound is MS. If the parameter is in the range of 5.495 Å to 5.505 Å, a zero-gap between the spin-up channel in the valence band and spin-down channel in the conduction band appears; the compound is SGS. If the parameter is in the range of 5.505 Å to 6.05 Å, the compound is HM, while for lattice constants larger than 6.05 Å, the compound is metal. These results are illustrated in Figure 9.

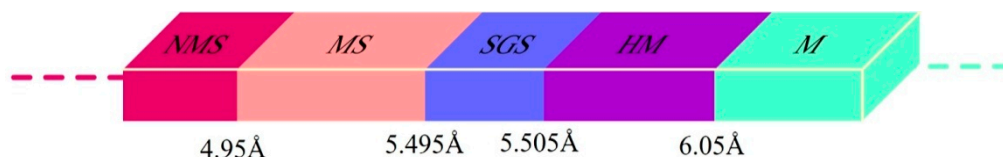


Figure 9. Physical transitions under uniformly strained lattice constants.

4. Conclusions

Using first-principle calculations, the crystal structure, band structure, magnetic properties, and origin of the band gap of the ScFeRhP compound were studied. The compound is HM at its equilibrium lattice constant. Upon introduction of strain, the compound exhibited transitions of its physic state (NMS \rightarrow MS \rightarrow SGS \rightarrow HM \rightarrow M), which implies that the magnetic properties and electronic structure could be widely changed by external tension or compression. A SGS feature appeared by tuning the lattice constant of the ScFeRhP compound. This study indicates that the ScFeRhP EQH compound can be used in spintronic applications.

Author Contributions: Y.G. conceived and designed the studies; Z.C. performed the calculations; H.R. and H.X. analyzed the data; Z.C. wrote the paper.

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