

Article

An Insight of the Theoretical Physics of Ru-Alloyed Iron Pyrite Studied for Energy Generation

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Abstract: Pyrite FeS₂ has become the focus of many researchers in thin-film photovoltaics because it has some possibilities in photovoltaics. In this manuscript, we present an experimental and a theoretical study of the electronic structure of pyrite FeS₂ alloyed with a small concentration of 1.19% of ruthenium (Fe_{0.9881}Ru_{0.0119}S₂) by using the Linear Muffin-Tin Orbital Method in the Atomic-Sphere approximation (LMTO-ASA) calculations and the density of states. We observed that the bandgap of FeS₂ increases from 0.90508 to 1.21586 eV when we replace ~1.19% of the Fe atoms with ruthenium atoms ($x = 0.0119$ concentration of Ru). We prove that this low concentration of Ru saved the gap states and the electronic and optical properties of FeS₂ pyrite. Our calculated electronic bandgap is 1.21586 eV and direct. Our results confirm that the symmetric operation of the space T_h⁶ (Pa3) saves electronic structure of iron pyrite when alloyed with ruthenium.

Keywords: bandgap; iron pyrite; spray pyrolysis; photovoltaic cell



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1. Introduction

Our work is inspired by the fact that making photovoltaic cells is an interest of many researchers and this is due to the fact that these cells are used in renewable energy. So, finding a low-cost and abundant material that can be used in making such cells is very important and interesting work.

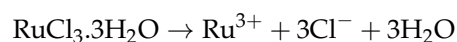
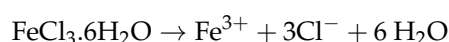
Iron pyrite FeS₂ is very important among metal sulfide minerals which is recently in the focus of experimental interest because of its high abundance, its low cost, its nontoxic constituent elements, and high light absorption coefficient ($\sim 10^5 \text{ cm}^{-1}$ for $h\nu > 1.4 \text{ eV}$), see [1,2]. This interesting material has been the major interest of many researchers in the field of photovoltaics because it is a promising material for photovoltaic cells [3–17]. It has been proven that the Solid State Schottky solar cells and pyrite photoelectrochemical cells (PEC) have large short-circuit current densities ($30\text{--}42 \text{ mA cm}^{-2}$) and quantum efficiencies (up to 90%) [1,2]. Iron pyrite is a semiconductor which has a bandgap of 0.95 eV [3] which is relatively small for solar cell applications. Therefore, it is essential to introduce suitable techniques to enlarge this bandgap of iron pyrite to develop pyrite-based photovoltaic cells and photoelectrochemical solar cells. The bandgap of FeS₂ pyrite can be enlarged by adding the anions of FeA_xS_{2–x} (where A is an anion element such as As, O, etc.) or cations Fe_{1–x}M_xS₂ where M is a cation element such as Zn, Ru, etc.). These alloying techniques have been used extensively, see [18,19]. Anion alloying of FeS₂ with oxygen has been proven to increase its bandgap [20]. Furthermore, Sun in [18] claimed that FeS₂ pyrite alloys with Os and Zn increases the bandgap from 0.95 eV to 1.2–1.5 eV. One of the elements that can alloy with FeS₂ pyrite to increase its bandgap is Ruthenium (Ru). Ru is an element that has been used widely for alloying and surface-coating of N-Chlorosuccinimide (NCS) due to its stability.

Ruthenium sulfide (RuS_2) has a bandgap of 1.8 eV [21], hence, the bandgap of Ru-alloyed FeS_2 pyrite, $\text{Fe}_{1-x}\text{Ru}_x\text{S}_2$, can be increased from 0.95 to 1.8 eV if we can reach the whole alloying composition range. Sun and Ceder [22] calculated the bandgap of pyrite $\text{Fe}_{1-x}\text{Ru}_x\text{S}_2$ and $\text{Fe}_{1-x}\text{Os}_x\text{S}_2$ using density functional theory (DFT). They showed that it is possible to enlarge the bandgap of FeS_2 pyrite if some Fe is replaced by Os or Ru. Jun Hu et al. [18] studied iron pyrite alloyed with oxygen by DFT calculation; their calculated bandgap shows an increase from 1.02 eV to 1.52 eV. FeS_2 pyrite has a direct bandgap [23–26], while RuS_2 has an indirect bandgap [27–30]. Until now, determining the properties (optical and electric) of FeS_2 pyrite alloying with ruthenium (Ru) has been inconclusive. Ouertani et al. [23] found that the gap of Ru-alloy can increase to 1.31 eV with a direct bandgap. There is also some new theoretical work done in [31]. In this manuscript, we used the Linear Muffin-Tin Orbital Method in the Atomic-Sphere approximation LMTO-ASA calculation to study the effect of small concentrations of 1.9% of Ru on the bandgap, electronic structure, and optical properties of FeS_2 pyrite because LMTO-ASA is imperative for calculations of the ground-state properties of compounds. It includes the effect of charge transfer which is expected to provide the main uncertainty in energy band calculations for compounds.

2. Experimental

2.1. Materials and Method

We used spray pyrolysis for fabrication of our sample. In our procedures, we chose of a solution obtained from the dissolution of 8.3 g of $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ with a molar ratio as $\text{FeCl}_3 \cdot 6\text{H}_2\text{O} : \text{RuCl}_3 \cdot 3\text{H}_2\text{O} = x:1 - x$ ($x = 0.0119$) through 10 min substrates and heated at 370 °C. The transport rate is about 70 cm and 7 mL/min. In the aqueous solution, we have the following reactions:



We obtained $\text{Fe}_{0.9881}\text{Ru}_{0.0119}\text{S}_2$ phases in our Iron pyrite layers.

2.2. Characterization Techniques

The crystal structures of $\text{Fe}_{0.9881}\text{Ru}_{0.0119}\text{S}_2$ are studied by XRD (X-ray diffraction) by using Phillips D500 powder with $\text{CuK}\alpha$ radiation at $\lambda = 1.42$ Å. The XRD patterns is shown in Figure 1. Representative diffraction peaks at $2\theta = 32.92$, 37.85, and 57.59 correspond to the (200), (210), and (311) planes. These lines were obtained by using powder diffraction data bases (JCPDS card n°: 00-36-1453). The resulting structure of $\text{Fe}_{0.9881}\text{Ru}_{0.0119}\text{S}_2$ is a cubic crystal structure belonging to the space group $\text{Pa}\bar{3}$ (205). Both Iron pyrite FeS_2 and Ruthenium sulfide RuS_2 have a pyrite $\text{Pa}\bar{3}$ space group structure with 5.419 Å and 5.635 Å as lattice constants, respectively. We determined the lattice parameter using the Rietveld method utilizing the PDXL program.

Moreover, this Ru-alloyed iron sulfide ($\text{Fe}_{0.9881}\text{Ru}_{0.0119}\text{S}_2$) exhibits cubic crystal structure in the pyrite phase. The lattice constant and the atomic positions are presented in Table 1. The pyrite structure of $\text{Fe}_{0.9881}\text{Ru}_{0.0119}\text{S}_2$ was presented in a cubic crystal, by replacing one Fe atom with an Ru atom in metal positions and eight positions of sulfur atoms.

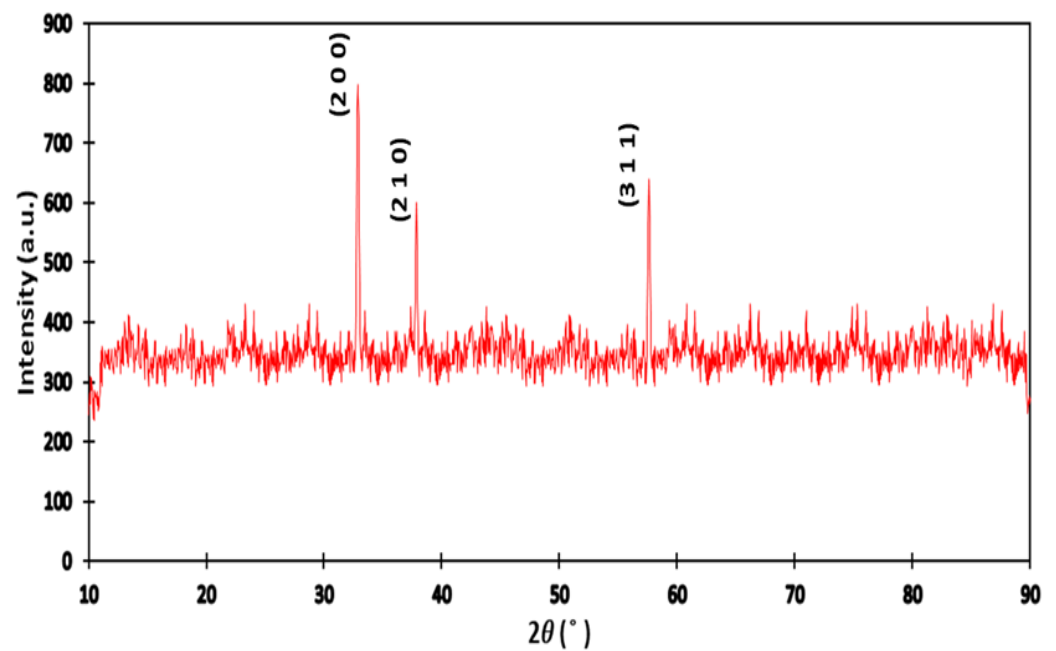


Figure 1. XRD spectrum for $\text{Fe}_{1-x}\text{Ru}_x\text{S}_2$ for $x = 0$ and $x = 0.0119$.

Table 1. Cell Parameters.

Cubic lattice a	5.517 Å
v (Position parameter)	0.113
u (Suffer position)	0.387
Bond length $d_{\text{S-S}}$	2.1212 Å

Note that compared to the pure Iron pyrite [24], we can see that the distance $\text{S} - \text{S}$ is similar to one in the S_2 molecule and the lattice constant increases because Ru ions are larger than Fe ions.

The optical absorption diagram of $\text{Fe}_{0.9881}\text{Ru}_{0.0119}\text{S}_2$ was carried out using a SHIMADZU 3100s spectrophotometer. Figure 2 shows $(\alpha h\nu)^2$ versus the photon energy $h\nu$ and Figure 3 shows $(\alpha h\nu)^{\frac{1}{2}}$ versus $h\nu$. The two graphs indicate that $\text{Fe}_{0.9881}\text{Ru}_{0.0119}\text{S}_2$ has a direct bandgap energy of 1.23 eV.

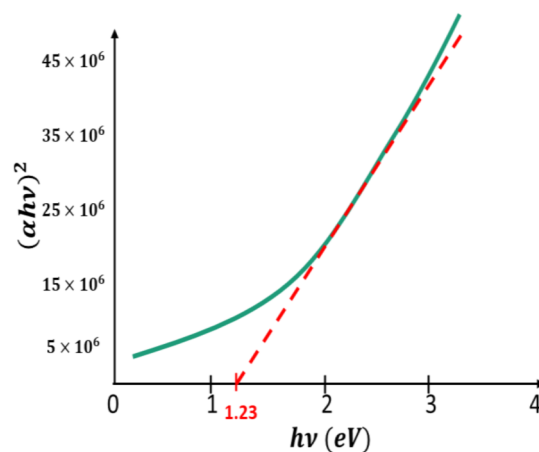


Figure 2. $(\alpha h\nu)^2$ versus $h\nu$ gives straight line, suggesting that the Ru -alloyed FeS_2 films have a direct band gap energy.

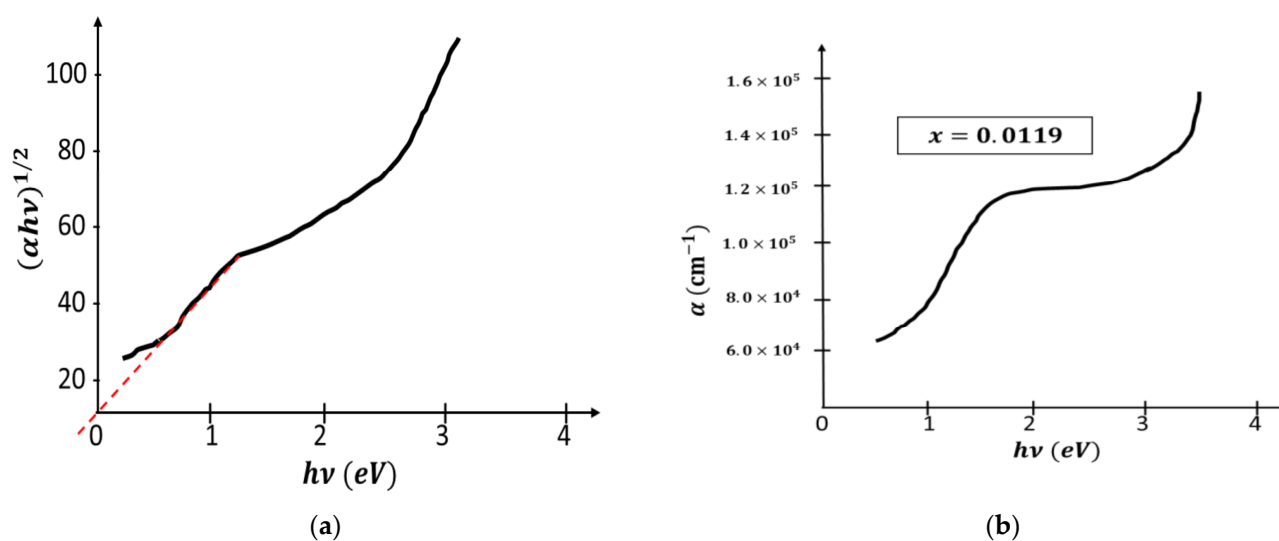


Figure 3. (a): $(\alpha h\nu)^{1/2}$ versus $h\nu$. (b): α versus $h\nu$.

Figure 3b shows the plot of absorption coefficients versus $h\nu$ and we note that the absorption coefficients are always high ($\alpha > 1.2 \times 10^5 \text{ cm}^{-1}$), which encourages their use in the photovoltaic domain.

3. Calculated Band Energy of $\text{Fe}_{0.9881}\text{Ru}_{0.0119}\text{S}_2$

3.1. Method

In our calculations, we apply the LMTO ASA method which has been explained in detail in several reports [32–34]. In our system, we have four metal atoms and eight sulfur atoms. In our case, the percentage of Ru is about 1.19% and is 25% lesser than that we have for one Ru atom and three Fe atoms and eight sulfur atoms. The data of sample are listed in the following Table 2:

Table 2. Sample Parameters.

Cubic lattice a	5.517 Å
ν (Position parameter)	0.113
u (Suffer position)	0.387
Fe position	(0.5 0.5 0), (0 0.5 0.5), (0.5 0 0.5)
Ru position	(0 0 0)
Bond length $d_{\text{s-s}}$	2.1212 Å

In our calculations, we employ the self-consistent band calculations. This is because it is a first-principles calculation where the density functional theory was used, see [35], using the local density approximation, see [36], and using numerical techniques which rely on the electron ion's treatment of interaction in the pseudopotential approximation [31]. However, the ASA Hamiltonian is completely specified by the potential parameters. It will generate moments from the eigenvectors of the Hamiltonian. For a certain potential, there is a unique correspondence between the logarithmic derivative D_ν at the sphere radius and the energy E_ν of the wave function φ . In principle, it is possible to specify either one. The potential P becomes simple because we use [37,38]

$$P(\epsilon) = \text{const} \frac{D(\epsilon) + 1 + 1}{D(\epsilon) - 1} \approx \left(\frac{\Delta_l}{\epsilon - C_l} + \gamma_l \right)^{-1}$$

where C_1 , Δ_1 , and γ_1 , are the “potential parameters” that parameterize P . C_1 corresponds to the band “center of gravity”, Δ_1 is the “band width” parameter which corresponds approximately to the bandwidth of that l channel if it were uncoupled from the other l channels, and γ_1 is the “band distortion parameter” which describes the deformations relative to a universal shape. Generally, a small parameterization is a perfect method to study a band structure. First, we obtain the potential parameter for all atomic spheres. The muffin-tin potential constant V_{MTZ} around Fe, Ru, and S is equal to -0.835283 . We have 24 symmetry operations. The muffin-tin MT radii are 2.939 a.u. for Ru, 2.951 a.u. for Fe, and 2.202 a.u. for S. The initial sphere packing was equal to 79.2%, scaled to 87.9%. The role of these empty spheres is to reduce the number of iterations in this procedure and to reduce the overlap between the spheres centered at Fe, Ru, and S.

3.2. Band Structure

Figure 4 represents energy band structure of $\text{Fe}_{0.9881}\text{Ru}_{0.0119}\text{S}_2$. It shows all details of the valence and conduction bands in an energy range between -20 eV and $+8$ eV. Different colors are used to describe this band structure to indicate the contributions of the cations (Fe and Ru) and the anion (S). We have five distinct groups based on the order of increasing energy of this band structure. Note that the occupied bands have 80 valence electrons. First, we can see that the first two groups of bands (I, II) are associated with bonding and antibonding pairs of orbitals on S_2 pairs. The two groups have a maximum energy of -11 eV and their character is $\text{S}3s$, where $\text{S}3s$ states are predominant. The structure of sulfur $3p$ states start approximately at -7 eV; their basic states include an extra structure due to the Fe $3d$ levels and a small admixture of Ru $4d$ levels. This group composes with bonding $\text{S } 3p$ and Fe e_g and Ru e_g . The Fe $3d t_g$ and Ru $4d t_g$ bands, which give us the fourth group of bands (IV), are under the Fermi level. Note that, above the Fermi level, we have a split of conduction bands; these bands have $\text{S } 3p$ and Fe $3d e_g$ and Ru $4d e_g$ characters, due to the group V.

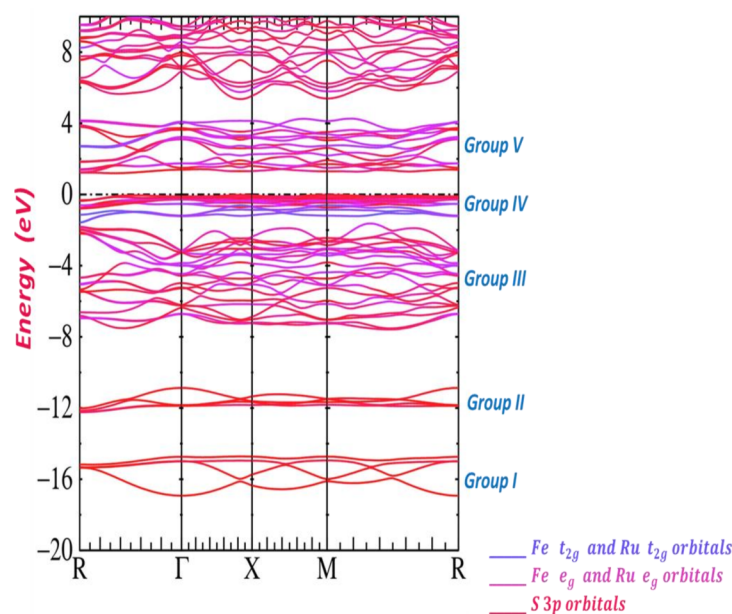


Figure 4. Band structure of $\text{Fe}_{0.9881}\text{Ru}_{0.0119}\text{S}_2$.

Our calculations indicate that $\text{Fe}_{0.9881}\text{Ru}_{0.0119}\text{S}_2$ is a direct gap semiconductor of 1.21586 eV. The valence band maximum (VBM) is -0.055993 Ry (-0.761823 eV), and the conduction band minimum (CBM) is 0.033408 Ry (0.454539 eV). The Fermi energy of -0.055993 Ry (-0.761823 eV) is very close to the maximum valence band, which leads us to deduce that we have an empty conduction band and a filled valence band. Thereby, we can conclude that our bandgap of $\text{Fe}_{0.9881}\text{Ru}_{0.0119}\text{S}_2$ is direct at the Gamma point (Γ).

Figures 2 and 3 show that the optical measurement of $\text{Fe}_{0.9881}\text{Ru}_{0.0119}\text{S}_2$ has a direct gap of 1.23 eV, which is in good agreement with our calculations.

Figure 5a presents the band structure of FeS_2 pyrite obtained by LMTO-ASA. Our calculation indicates that FeS_2 pyrite is a direct-gap semiconductor, with a calculated gap of 0.90508 eV. The valence-band energy (ev) is -0.000533 Ry, and the energy of the conduction band (ec) is 0.066017 Ry. The Fermi energy -0.000533 Ry matches the valence-band energy, which indicates that the valence band is filled while the conduction band is completely empty. Consequently, our bandgap of FeS_2 is direct at the Γ gamma point. The optical measurement of FeS_2 pyrite has a direct gap of approximately 0.95 eV [24], in good agreement with our calculation.

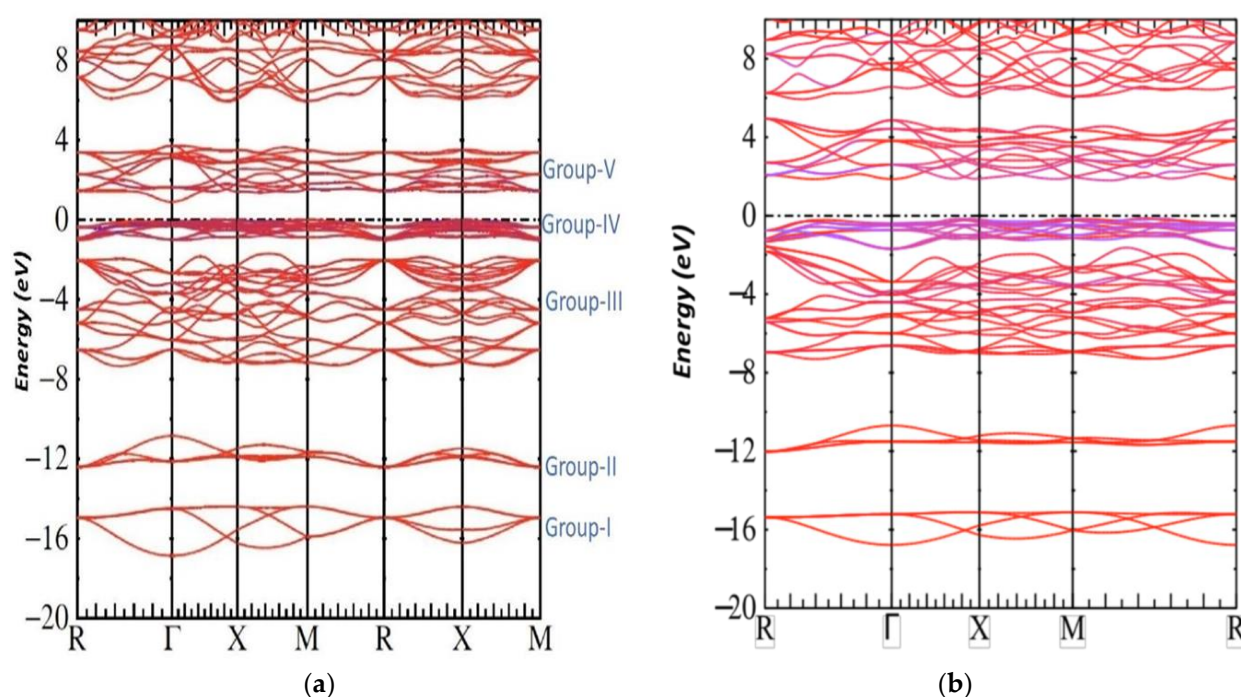


Figure 5. (a): Band structure of FeS_2 pyrite. (b): Band structure of RuS_2 pyrite.

Figure 5b is a structure of RuS_2 pyrite obtained by LMTO-ASA. Moreover, our figures indicate that RuS_2 has a bandgap semiconductor. The max valence band is at X, and the min conduction band is at Γ . The indirect bandgap is between X and gamma Γ , and the direct transition at Γ . We found the indirect bandgap has the following value: 1.80727 eV. The values of the filled bands encountered (ev) is about -0.126036 Ry and the empty bands encountered (ec) is about 0.006851 Ry. The Fermi energy is about -0.126036 Ry. Our obtained gap energy by the linear muffin-tin is in a good agreement with an experimental bandgap of 1.8 eV [27]. Note that the band structure of $\text{Fe}_{0.9881}\text{Ru}_{0.0119}\text{S}_2$ is similar to the band structure of FeS_2 pyrite and that is due to the fact that both have a direct bandgap and five groups of energy levels.

Figure 6 shows the energy diagram for Ru 4d, Fe 3d, and S 3p orbitals under the influences of crystal field splitting (CFS) and S-S dimerization. The bandgap E_g is denoted by the green arrow. The 3d and 4d orbitals of Fe and Ru are split into t_{2g} and e_g groups, while the 3p orbitals of S are split into $\text{PP}\sigma$, $\text{PP}\pi$, $\text{PP}\pi^*$ and $\text{PP}\sigma^*$ groups. This indicates that the CBM of $\text{Fe}_{0.9881}\text{Ru}_{0.0119}\text{S}_2$ alloy shifts upward toward the Fe e_g band, the CBM still originates from $\text{PP}\sigma^*$.

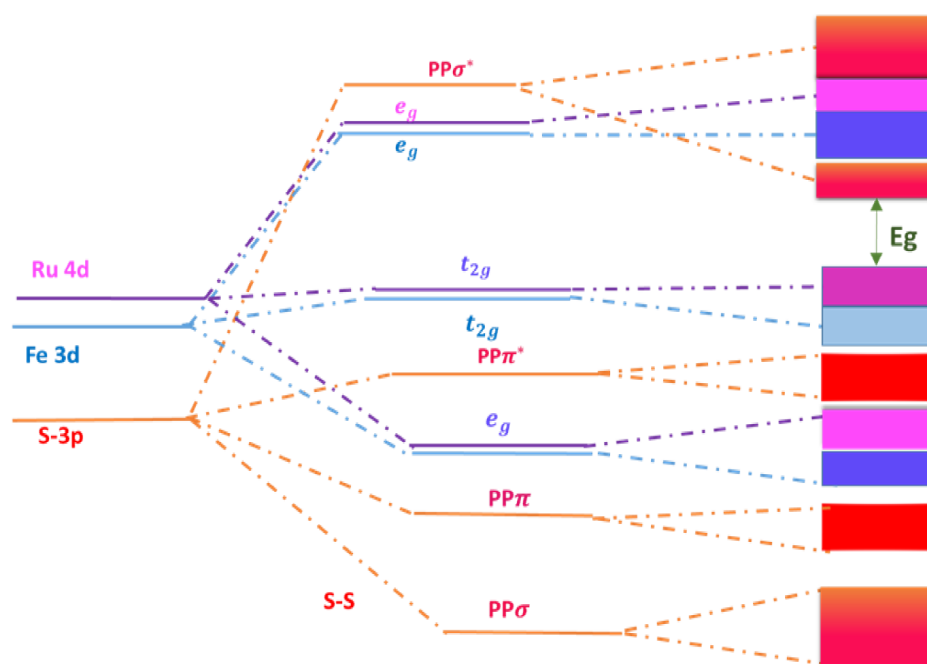


Figure 6. Energy diagram for orbitals.

The density of states (DOS) calculated below and above the Fermi level for $\text{Fe}_{0.9881}\text{Ru}_{0.0119}\text{S}_2$ is presented in Figure 7, in which a clear hybridization between Fe, Ru, and S states is clearly seen. The two smallest peaks around -1.2 Ry and -0.8 Ry show that the S contributions are dominant. Note that the valence bands of the first two groups (I and II) are the lowest. Fe and Ru in the third group (III) have a small contribution dominance, which is mostly dominant by S. The third and the fourth groups (III, IV) are between -0.6 Ry and -0.05599 Ry. In addition, in the fourth and the fifth groups (IV, V), Fe and Ru have a dominant contribution. The highest peak in group IV lies between -0.2 Ry and -0.055993 Ry below but very close to the Fermi level, which shows that the level t_{2g} is filled and all S 3p, Fe t_{2g} and Ru t_{2g} states (group IV states) are occupied. Hence, all S 3p and Fe e_g and Ru e_g states (group V) are empty indicating unoccupied e_g states.

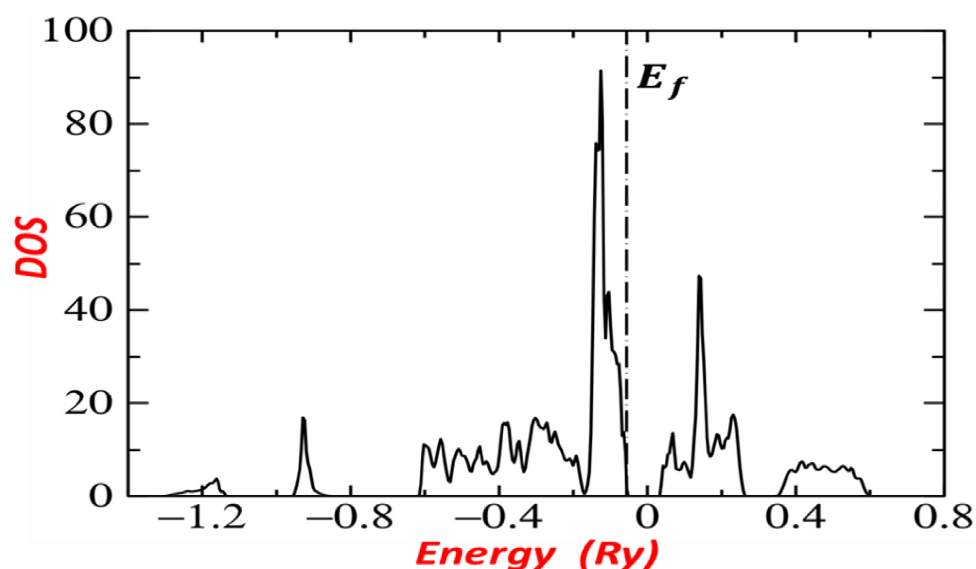


Figure 7. Density of states of $\text{Fe}_{0.9881}\text{Ru}_{0.0119}\text{S}_2$.

In summary, the valence bands are almost completely driven from the t_{2g} orbitals while the conduction band is almost pure Sp. In Figure 4, it can be clearly seen that the bottom of the conduction band is red (the S 3p states) and that the conduction band is similar to that of Iron pyrite [24]. We conclude that the presence of a low concentration of 1.19% of Ru alloy will shift the bandgap up by ~ 0.4 eV; at the same time, it does not change the state of Iron pyrite. Furthermore, our calculated bandgap of 1.21586 eV is in very good agreement with the experimental value 1.23 eV.

4. Conclusions

An adequate molar ratio was chosen to fabricate $\text{Fe}_{0.9881}\text{Ru}_{0.0119}\text{S}_2$ thin films having good properties for solar cell application. We have investigated the electronic structure of $\text{Fe}_{0.9881}\text{Ru}_{0.0119}\text{S}_2$ using LMTO-ASA calculations. We showed that substituting ruthenium for Fe atoms is a good method to enlarge the bandgap of FeS_2 pyrite while saving gap states and the optical and electrical properties of FeS_2 pyrite. The small concentration of 1.19% of Ru alloy raises the maximum of the conduction band by 0.3 eV, which is considered as a desired bandgap value for solar cell applications. We note that it is highly possible to use $\text{Fe}_{0.9881}\text{Ru}_{0.0119}\text{S}_2$ as multispectral photovoltaic cells (1.2–1.3 eV).

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