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# Discovery of new potential magnetic semiconductors in quaternary Heusler compounds by addition of lanthanides

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Magnetic semiconductors have attracted a lot of attention by having both electronic charge and spin degrees of freedom. In this paper, we obtained twenty magnetic semiconductors such as FeVLaSb, FeVPrSb, FeCrTbSi, CoVDySi, and CoVHoSi by adding lanthanides to quaternary Heusler compounds based on the Slater–Pauling law and orbital hybridization theory. The relationship between the lattice constants and energy gaps of the magnetic semiconductors with lanthanide elements is investigated by in-depth analysis. These magnetic semiconductors of quaternary Heusler compounds are promising candidates to find applications as spin filtering materials in spintronics devices.

**Keywords:** magnetic semiconductor, rare-earth element, quaternary Heusler compounds

**PACS:** 75.50.Pp, 72.20.Ee, 71.20.Nr **DOI:** 10.1088/1674-1056/acfaf7

## 1. Introduction

Recently, the research on magnetic materials has become a key object in the field of advanced technology, and spintronics has become the main research hotspot of magnetic materials.[1,2] Successful injection of spin-polarized currents into semiconductors has been one of the problems that spintronics needs to solve, and the most likely solution to this problem is spin filtering materials (SFMs).[3–5] SFMs are supposed to be magnetic semiconductors and the main research hotspots for magnetic semiconductors are two types of semiconductors, one is dilute magnetic semiconductors (DMS) and the other is ferromagnetic semiconductors.[6,7] DMS are both semiconductor and magnetic which makes them attractive for research. DMS have received a lot of attention from researchers because of their ability to handle charge and spin. However, DMS technology is still in the research stage and needs further study.[8,9]

Heusler compounds are known for their high spin polarizabilities and their Curie temperatures ($T_C$) can considerably exceed room temperature.[10] Due to this unique combination of properties, high $T_C$ spin filter materials can be developed using Heusler compounds. However, further studies are needed to fully understand and exploit their potential.[11,12] Since quaternary Heusler compounds have many possibilities, the study of quaternary Heusler compounds has revealed many interesting things that we should learn more about quaternary Heusler compounds.[13–15] In Wang's report,[16] several quaternary Heusler compounds such as FeVNbAl and FeCrScSi are magnetic semiconductors.

In order to predict the special properties of Heusler compounds, the theory of orbital hybridization is needed. In the Galanakis' analysis of full-Heusler compounds, they concluded that the energy gap in the energy band of full-Heusler compounds with 24 valence electrons comes mainly from orbital hybridization between the atoms at the $A$ and $C$ positions.[17,18] Similarly, this conclusion can be extended to the quaternary Heusler compounds of the 21-valence electron system because they have the same space group and similar structures.[19] So far, many quaternary Heusler compounds have been predicted as magnetic semiconductors. According to the generalized Slater–Pauling rule, the quaternary Heusler compounds in 21 valence electrons are more promising as magnetic semiconductors.[20]

Figure 1(a) shows a schematic diagram of the Heusler compound with four points along the diagonal lines $A$, $B$, $C$ and $D$. The coordinates of the four points are $A$ (0,0,0), $B$ (0.25,0.25), $C$ (0.50,0.50,0.50), and $D$ (0.75,0.75,0.75). The quaternary Heusler compound $XX'YZ$ is a LiMgPdSb-type compound with space group $F$-43$m$, number 216.[21,22] According to Wang's report,[16] the transition metal atom $X$ atom occupies position $C$, the transition metal $X'$ atom occupies position $A$, the lanthanide element atom $Y$ occupies position $B$ and the main group element $Z$ occupies position $D$. This station has the lowest energy and the most stable structure. Figure 1(b) shows the density of states (DOS) diagram of a spin gapless semiconductors (SGS) with a zero band gap in the spin-up direction and a wider band gap in the spin-down direction.[23,24] Figure 1(c) shows the DOS diagram of the magnetic semiconductor.[16]

Based on this conclusion, we obtained 20 magnetic semiconductors by changing the atoms at position $B$ and replacing them with atoms of the lanthanides without changing the

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atoms at positions *A* and *C*, keeping the total number of electrons at 21. We demonstrated that these compounds are all magnetic semiconductors under equilibrium lattice constants. It is worth noting that these magnetic semiconductors have certain band gap characteristics in their energy bands and DOS. In further research, it was found that the spin up, spin down, and total energy gap of these magnetic semiconductors have clever relationships with lattice constants.

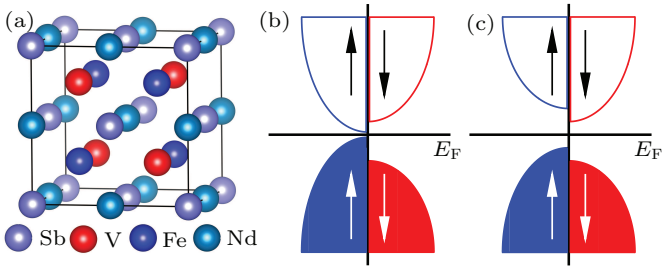



**Fig. 1.** (a) Schematic illustration of the Heusler compound. (b) DOS of SGS. (c) DOS of magnetic semiconductors.

## 2. Computations details and methods

VASP is a software package developed by the Hafner group at the University of Vienna to perform electronic structure calculations and quantum molecular mechanics dynamics simulations.[25–27] The structural model is processed by VESTA and the equilibrium lattice constants are obtained by VASP first-principles calculations. All calculations are based on the equilibrium lattice constants using a Gamma scattering point approach with a $14 \times 14 \times 14$ *k*-point grid for Brillouin zone integration in quaternary Heusler compounds.[28] The cut-off energy is 600 eV and the convergence criterion is $1 \times 10^{-6}$ eV. The density functional theory (DFT) is used to calculate the total ordered structure and the generalized gradient approximation (GGA) is used to correct the functional. The projected augmented wave (PAW) is used to describe the atom.[21,22,29]

## 3. Results and discussion

Here for the sake of searching for magnetic semiconductor, one should take into account orbital hybridizations of both the spin-up and spin-down directions. We provide a schematic of hybridization in Fig. 2. The hybridization process can be known from reference,[27] where the sp atom produces one s-band and three p-bands. $X_A$ atoms produce d-orbital hybridization with $X'_C$ atoms and after the completion of hybridization $X_A$–$X'_C$ undergoes d-orbital hybridization with $Y_B$ atoms. Then one s-band, three p-bands, two degenerate $e_g$, three degenerate $t_{2g}$ and three degenerate $t_{1u}$ are obtained after the completion of hybridization. The f orbital electrons are placed in the core because these electrons are relatively localized and generally difficult to interact with electrons from other atoms. The majority spin energy band in 21 valence electrons Heusler compounds usually has 12 valence electrons, which can fully occupy $t_{1u}$. But the minority spin energy band has only 9 valence electrons which makes $t_{1u}$ empty. When the number of spin-up and spin-down electrons is asymmetrical and the Fermi level crosses the band gap between hybrid orbitals, this filling brings in energy gap and magnetism. So the Heusler compound in the 21-valence electron system is more likely to be magnetic semiconductors.[30]

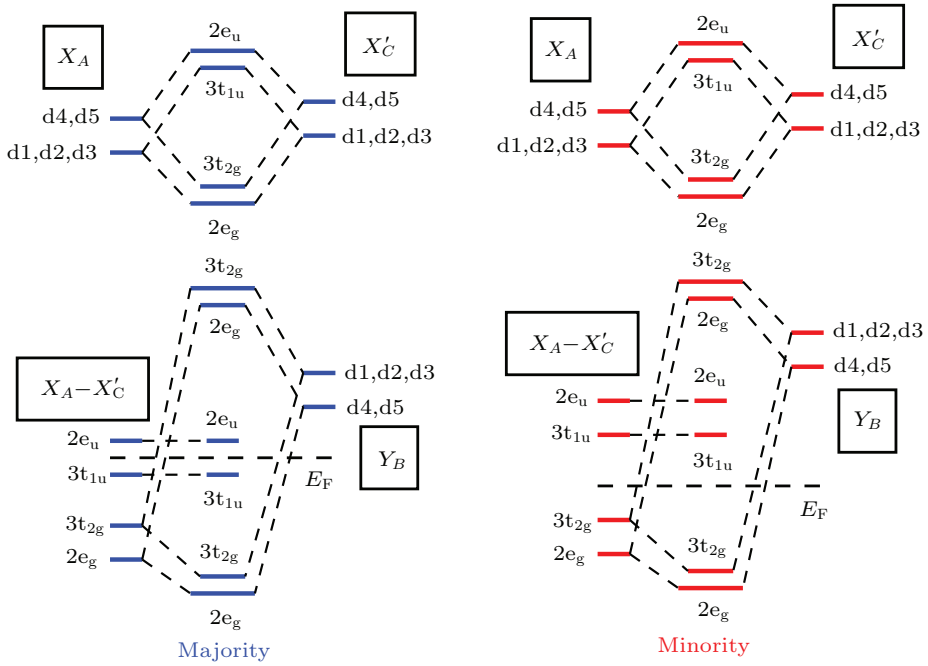



**Fig. 2.** Schematic diagram of the energy levels of the majority and minority spin electric band structure for the 21 valence electrons semiconductor.

In order to better explain the orbital hybridization theory, we calculated the energy bands and PDOS of FeVNdSb as shown in Fig. 3, where the Fermi level cross majority spin energy band of $t_{1u}$ and $e_u$. The Fermi level cross minority spin energy band of $t_{1u}$, so the spin-down energy gap is much larger than the spin-up energy gap and the total energy gap has 0.38 eV. The partial DOS of each element is shown in Fig. 4, where mainly $X$ and $X'$ play a dominant role near the Fermi level, and the PDOS of the lanthanide element $Y'$ is lower than $X$ and $X'$ at the Fermi level compared with the 3d group elements. From Fig. 4 we know that the bonding states of Fe atoms are mainly distributed in the range of −2 eV to 2 eV and that the bonding states of V atoms are similar to those of Fe atoms because of the hybridization between them. In this respect the atoms of the lanthanides provide the mobile electrons near the Fermi level, while Fe and V are responsible for providing the fixed domain states.

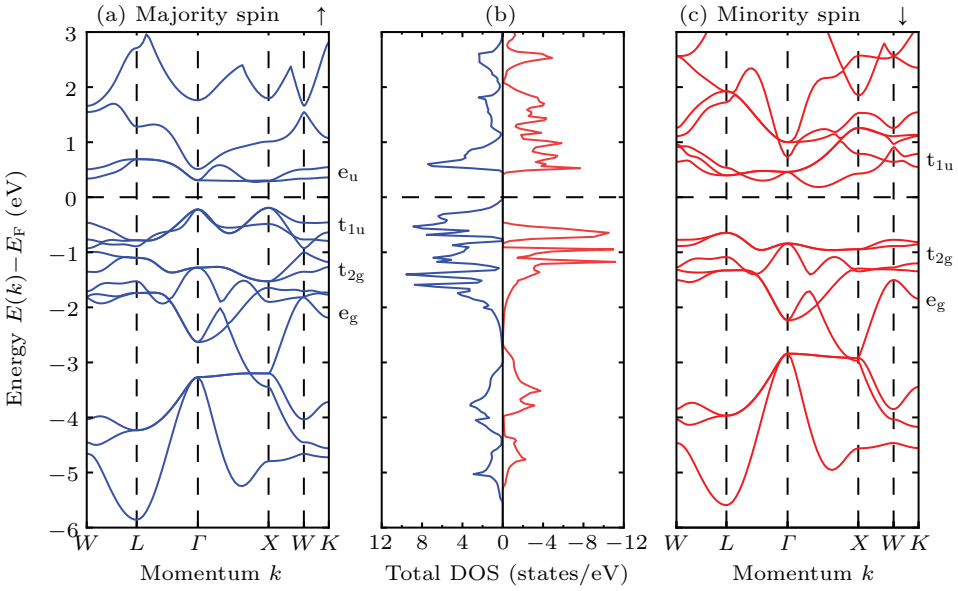



**Fig. 3.** Partial energy band structure and DOS of FeVNdSb: (a) majority spin; (b) DOS; (c) minority spin.

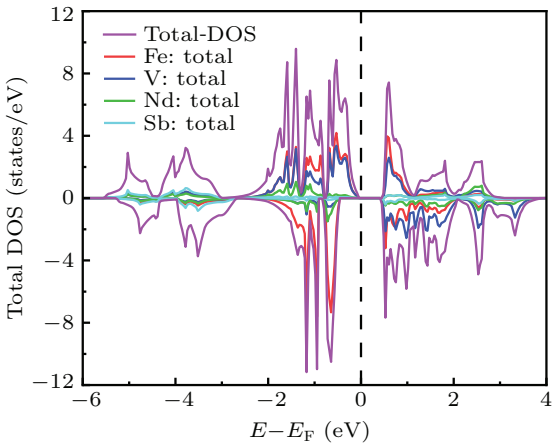



**Fig. 4.** PDOS of FeVNbAl, with different colored lines to plot the contribution of majority spin and minority spin to the total DOS.

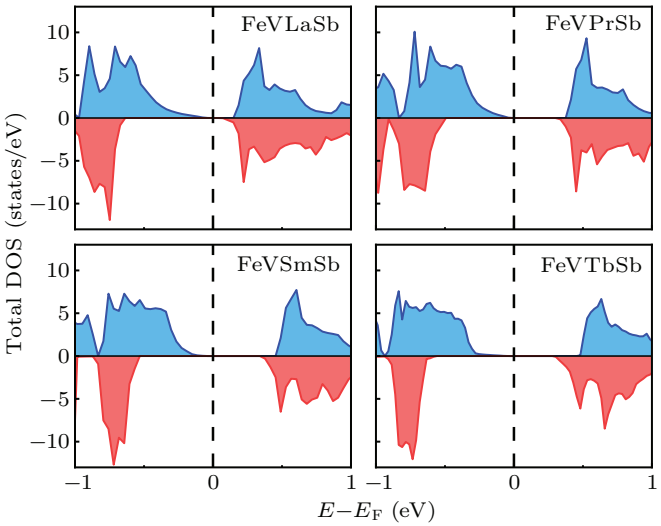



**Fig. 5.** The partial DOS of FeV$Y$Sb ($Y$ = La, Pr, Sm, Er). Blue filled represents majority spin, and red filled represents minority spin.

Next, the DOS diagrams and partial band structures of FeVLaSb, FeVPrSb, FeVNdSb, and FeVSmSb were calculated and compared with magnetic semiconductor FeVNdSb. As shown in Figs. 5 and 6, all quaternary Heusler compounds in the spin-up and spin-down directions have different band gaps and the energy bands are consistent with the DOS. Among the quaternary Heusler compounds, FeVLaSb has smaller spin-up and spin-down energy gaps.

It seems that the lanthanides play a very important role in the formation of magnetic semiconductors. In the quaternary Heusler compounds we calculate, replacing the corresponding atoms with lanthanides results in better energy bands and DOS, facilitating the formation of semiconductors. We have found a total of 20 magnetic semiconductors by replacing the lanthanides. Table 1 presents detailed data for the 20 magnetic

semiconductors. Comparing these magnetic semiconductors, we find a special relationship between the energy gap and the lattice constant. When replacing the lanthanide La with other elements of the same period, the spin-down and spin-up energy gaps increase presumably due to a decrease in the lattice constant. Magnetic semiconductors with grand energy gaps are more easily produced by the addition of lanthanide elements.

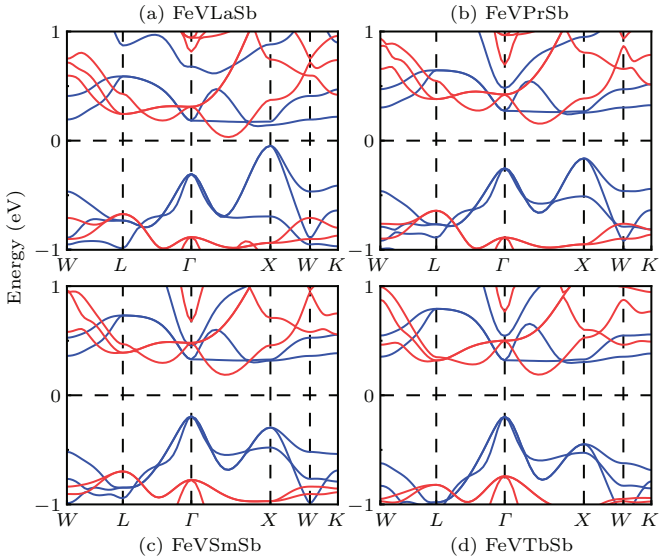



**Fig. 6.** The partial energy band structures of FeV$Y$Sb ($Y$ = La, Pr, Sm, Er). Blue line represents majority spin, red line represents minority spin.

In order to investigate the relationship between lattice constant and band gap of lanthanide magnetic semiconductors. We draw the curve of the energy gap of CoV$Y$Si with the lattice constant. As shown in Fig. 7, the larger lattice constant of these magnetic semiconductors leads to the decrease of the spin-up and spin-down energy gaps, and the total energy gap also becomes smaller. The initial inference is that when the lattice constant increases, it leads to an increase in the atomic spacing. This increase causes a weakening of interatomic interactions or a weakening of bonds between atoms, which leads to a more metallic bias, reflected in a decrease in the energy gap. Based on this, we can achieve the modulation of the energy gap size by changing the lattice constant. Based on this, we can achieve the modulation of the energy gap size by changing the lattice constant. By regulating the energy gap, we can make the energy gap larger and turn materials that are not magnetic semiconductors into magnetic semiconductors. This will facilitate the discovery of more magnetic semiconductors.

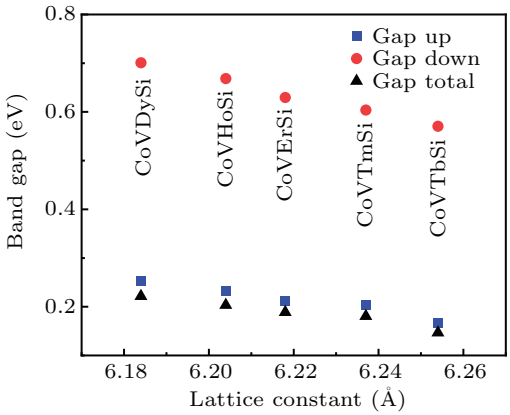



**Fig. 7.** The relationship between the energy gap and lattice constant of the magnetic semiconductor CoV$Y$Si ($Y$ = Tb, Dy, Ho, Er, Tm).

**Table 1.** The detail of all the magnetic semiconductors, a represents lattice constants, $R_Y$ represents lanthanide atomic radius, $M_{tot}$ represents total magnetic moments. Gap-up, Gap-down and Gap-total represent energy gaps of spin-up, spin-down and total.

| $XX'YZ$ | $a$ (Å) | $R_Y$ (Å) | $M_{tot}$ ($\mu_B$) | Gap-up (eV) | Gap-down (eV) | Gap-total (eV) |
|---|---|---|---|---|---|---|
| FeVLaSb | 6.423 | 1.061 | 2.586 | 0.1799 | 0.7051 | 0.0804 |
| FeVPrSb | 6.643 | 1.013 | 2.567 | 0.4033 | 0.7977 | 0.3182 |
| FeVNdSb | 6.677 | 0.995 | 2.565 | 0.4679 | 0.8309 | 0.3770 |
| FeVSmSb | 6.630 | 0.964 | 2.567 | 0.4945 | 0.8853 | 0.3816 |
| FeVTbSb | 6.572 | 0.923 | 2.697 | 0.4922 | 0.9307 | 0.3853 |
| FeVDySb | 6.557 | 0.908 | 2.682 | 0.4447 | 0.8295 | 0.3288 |
| FeVHoSb | 6.540 | 0.894 | 2.723 | 0.4838 | 0.8551 | 0.3512 |
| FeVErSb | 6.526 | 0.881 | 2.735 | 0.4769 | 0.8129 | 0.3314 |
| FeVTmSb | 6.510 | 0.869 | 2.742 | 0.4227 | 0.7783 | 0.3153 |
| FeCrGdSi | 6.252 | 0.938 | 2.923 | 0.1139 | 0.9041 | 0.1139 |
| FeCrTbSi | 6.233 | 0.923 | 2.932 | 0.1815 | 0.8507 | 0.1518 |
| FeCrDySi | 6.215 | 0.908 | 2.944 | 0.1790 | 0.7971 | 0.1790 |
| FeCrHoSi | 6.198 | 0.894 | 2.951 | 0.1657 | 0.7437 | 0.1657 |
| FeCrErSi | 6.178 | 0.881 | 2.960 | 0.1514 | 0.6890 | 0.1514 |
| FeCrTmSi | 6.165 | 0.869 | 2.967 | 0.1362 | 0.6361 | 0.1362 |
| CoVTbSi | 6.254 | 0.923 | 2.757 | 0.1659 | 0.5706 | 0.1468 |
| CoVDySi | 6.184 | 0.908 | 2.749 | 0.2521 | 0.7012 | 0.2217 |
| CoVHoSi | 6.204 | 0.894 | 2.768 | 0.2313 | 0.6684 | 0.2034 |
| CoVErSi | 6.218 | 0.881 | 2.788 | 0.2110 | 0.6296 | 0.1887 |
| CoVTmSi | 6.237 | 0.869 | 2.804 | 0.2038 | 0.6039 | 0.1806 |

## 4. Conclusions

In summary, by using first-principles calculations, the electronic structure, magnetic properties, and lattice constants versus the energy gap of newly designed Heusler compounds containing lanthanides have been investigated in this work. The calculation results indicate that these Heusler compounds are magnetic semiconductors under their equilibrium lattice constants. The size of the energy gap is adjusted by changing the lattice constants of these magnetic semiconductors and the study of lattice constants and energy gap relationships can help to expand the application of these magnetic semiconductors. We have discovered 20 magnetic semiconductors of Heusler compounds containing lanthanide elements. These findings provide a potential mechanism for finding more magnetic semiconductors. All these magnetic semiconductors containing lanthanide elements can be used as SFMs for spin electron applications.

## Acknowledgements

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