A first-principles study of rare earth quaternary Heusler compounds: RXVZ (R = Yb, Lu; X = Fe, Co, Ni; Z = Al, Si)

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Rare earth equiatomic quaternary Heusler (EQH) compounds with chemical formula RXVZ (R = Yb, Lu; X = Fe, Co, Ni; Z = Al, Si) have recently attracted much attention since these materials are easily prepared and they also provide interesting properties for future spintronic applications. In this work, rare Earth-based EQH compounds in three types of structures are theoretically investigated through first-principles calculations based on density functional theory. We find that most of the studied rare Earth EQH compounds exhibit magnetic ground states including ferro-, antiferro-, and ferri-magnetic phases. Owing to the nearly closed shell f orbital in Lu and Yb, the spin magnetic moments mainly come from the 3d transition metal elements. In particular, in the type I structure, a large portion (7 out of 12) of EQH compounds are ferromagnetic half-metals (HMs) with integer magnetic moments ranging from 1 to 3 µB. In the type II structure, YbFeVAl is found to be a rare case of antiferro-magnetic (AFM) half-metal with zero total magnetic moments. Surprisingly, we also discover an unusual magnetic semiconductor LuCoVSi in the type III structure with a total spin magnetic moment of 3.0 µB and an indirect band gap of 0.2 eV. The structural and magnetic stabilities such as formation energy, magnetization energy as well as the mechanical stabilities such as the bulk, shear, and Young’s moduli, and Poisson’s, and Pugh’s ratios of these EQH compounds are also investigated. Most of the studied compounds exhibit mechanical stability under the mechanical stability criteria and show elastic anisotropy. Our work provides guidelines for experimental researchers to synthesize useful materials in future spintronic applications.

I. Introduction

It is well known that Heusler compounds are intermetallic materials with rich magnetic properties.1–7 Since the first discovery of the Cu2MnSn Heusler alloys in 1903, Heusler compounds have become interesting and promising materials in both theoretical and experimental research fields. To date, thousands of members of Heusler compounds have been discovered with a wide range of physical properties, such as half-metals, ferrimagnets,8–10 ferromagnets,11–13 shape memory alloys,14,15 and even tunable topological insulators.16,17 These properties are related to a high potential for spintronics, energy technologies, and magneto-caloric applications. The typical Heusler compounds are ternary alloys that have the chemical formula X2YZ and crystallize in the cubic L21 structure (space group Fm3m), where X and Y are different transition metal elements, and Z is an sp/main-group (group III, IV, or V) element.8,18 When one of the X’s is substituted with a different transition metal M, a new equiatomic quaternary Heusler (EQH) compound with the stoichiometric composition of MXYZ (space group F43m) is formed.3,19,20

Half-metallic EQHs demonstrated through theoretical and experimental studies have attracted a lot of attention due to their superior magnetic and transport properties. Recently, some EQH compounds containing 4d transition metal elements or rare earth elements have been found to have intriguing properties.7,21 Some of them exhibit more robust half-metallic properties against interfering effect than general ternary Heusler alloys.22,23 Some of them are half-metallic magnets (HMMs) with larger spin–flip gaps than 3d transition metal based EQHs.24 Furthermore, some of EQHs are recently discovered as spin-gapless semiconductors (SGSSs), which possess important and unique properties as follows: (1) the electrons in the valence band need less energy to get excited to the conduction band; (2) the excited electrons and holes can be fully spin-polarized.
simultaneously; (3) through the Hall effect, fully spin-polarized electrons and holes will be separated easily.\(^2\) It is also proposed that HMMs with EQH structures have lower-power dissipation than ternary Heusler alloys due to less disorder.\(^3\)

As such, enormous attention has been devoted to searching for new spintronic materials through 4d transition metal/rare-earth element EQHs. In this work, we present a systematic theoretical investigation of the structural, electronic, magnetic, and mechanical properties of rare-earth-element-containing EQHs: YbXVZ and LuXVZ (X = Fe, Co, Ni; Z = Al, Si) based on first-principles density functional theory calculations. We demonstrate several intriguing phases such as ferromagnetic half-metal (HM), antiferromagnetic half-metal (AHM), and magnetic semiconductor (MSC) phases, which are important for future spintronics. In particular, since the latter two phases are rarely found, our work thus provides a good opportunity for experimentalists to pursue studies of such high-potential unusual materials.

II. Computational method

The ideal RXVZ (R = Lu, and Yb, X = Fe, Co, and Ni, Z = Si, and Al) full-Heusler alloys have the cubic L2\(_1\) structure with the point group 225 (Fm\(_{3m}\) symmetric) as shown in Fig. 1. It consists of four interpenetrating fcc lattices with R, X, V, and Z atoms located at (0, 0, 0), (1/4, 1/4, 1/4), (1/2, 1/2, 1/2), and (3/4, 3/4, 3/4), respectively. Following the previous study by Wang et al.,\(^2\) we assume that the rare earth element R sits at (0, 0, 0). Therefore, there are three possible structures for the equiatomic quaternary Heusler compounds. These three possible structures are depicted in Fig. 1. Note that the type III structure is similar to that of normal Heusler compounds, A\(_2\)BC, with A and B being transition metals and C being main group elements.

The structural, electronic, and magnetic properties of RXVZ Heusler alloys are calculated by using the density functional theory as implemented using the Vienna \textit{ab initio} simulation package (VASP).\(^26,27\) The Perdew–Burke–Ernzerhof (PBE) generalized gradient approximation (GGA) was chosen for the exchange and correlation functional.\(^26,29\) The \(\Gamma\)-centered Monkhorst–Pack scheme with a \(k\)-mesh of \(12 \times 12 \times 12\) is used for Brillouin zone integration. The self-consistent total energy convergence criterion is set to be \(1.0 \times 10^{-6}\) eV. In all cases, a plane wave basis set with a cut-off energy of 450 eV was used. The equilibrium lattice constant, \(a\), for all three types of structures is obtained using the structure optimization technique. The convergence criterion in the geometry optimization calculations was \(1.0 \times 10^{-6}\) eV. To calculate the total energy of the isolated atoms, we use a very large supercell with 20 Å of separation in all \(x\), \(y\), and \(z\) directions which should be wide enough to decouple the nearest atom. The electronic configurations used are 5p\(^6\)5d\(^2\) (Lu), 5p\(^6\)5d\(^2\) (Yb), 3d\(^4\)4s\(^1\) (V), 3d\(^7\)4s\(^1\) (Fe), 3d\(^8\)4s\(^1\) (Co), 3d\(^3\)4s\(^1\) (Ni), 3s\(^2\)3p\(^2\) (Al), and 3s\(^2\)3p\(^2\) (Si). Our calculated spin magnetization values for the Lu, Yb, V, Fe, Co, Ni, Al, and Si isolated atoms are 1.00 \(\mu_\text{B}\), 0.00 \(\mu_\text{B}\), 5.00 \(\mu_\text{B}\), 4.00 \(\mu_\text{B}\), 3.00 \(\mu_\text{B}\), 2.00 \(\mu_\text{B}\), 1.00 \(\mu_\text{B}\), and 2.00 \(\mu_\text{B}\), respectively.

III. Results and discussion

A. Electronic and magnetic properties

In order to ensure the suitability of the DFT-GGA approach for EQHs, we have analysed three compounds CoFeCrGe, CoFeMnGe, and CoFeTiAl, which have been prepared and measured successfully in experiments as benchmarks shown in Table 1. It is clear that the lattice constants and magnetic moments calculated by DFT-GGA are in good agreement with the previous experimental results, indicating that the DFT-GGA approach is reliable for these kinds of compounds.

Listed in Table 2 are the calculated lattice constants (Å), cohesive energy (eV f.u.\(^{-1}\)), and formation energy (eV f.u.\(^{-1}\)) of the rare Earth-based equiatomic Heusler compounds. The cohesive energy is calculated as the difference between the sum of the ground state total energies of the isolated atoms and the total energy of the quaternary Heusler compounds,
Factors such as pressure, temperature, and/or electromagnetic means that the synthesis of the material is dependent on extra conditions and the stability of the compound is lower than that of its individual components. The formation energy indicates that the total energy of the compound is lower than the sum of the individual components. 

### Table 1: Comparison of lattice constant (Å) and total spin magnetization \( m (\mu_B) \) between PBE-GGA calculated results and experimentally observed values.

| Compounds          | \( a_{\text{exp.}} \) (Å) | \( a_{\text{calc.}} \) (Å) | \( m_{\text{exp.}} (\mu_B) \) | \( m_{\text{calc.}} (\mu_B) \) |
|--------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|
| CoFeCrGe            | 5.77                        | 5.712                       | 3                           | 3                           |
| CoFeMnGe            | 5.76                        | 5.708                       | 4.2 (at 5K)                 | 4.015                       |
| CoFeTiAl            | 5.85                        | 5.798                       | 0                           | 0                           |

### Table 2: Calculated equilibrium lattice constant (Å), cohesive energy (eV f.u.\(^{-1}\)), and formation energy (eV f.u.\(^{-1}\)) of rare earth RXVZ compounds in three types of lattice structures.

| Lattice constant (Å) | Cohesive energy (eV f.u.\(^{-1}\)) | Formation energy (eV f.u.\(^{-1}\)) |
|----------------------|------------------------------------|-------------------------------------|
| X = Fe Co Ni         |                                    |                                     |

### Table 3: Calculated magnetic ground state, total spin moment \( (m_R) \) in \( (\mu_B) \) units, atomic spin moment \( (m_R, m_X, m_V, m_Z) \), and magnetization energy (eV f.u.\(^{-1}\)).

The magnetization energy is the energy difference between the magnetic and nonmagnetic phases. Previous studies\(^{23}\) show that type 3 is the most stable structure for LuCoVSi with the lattice constant and total magnetic moment of 6.26 Å and 3 \( \mu_B \) f.u.\(^{-1}\), respectively. Our calculated results of 6.207 Å and 3 \( \mu_B \) f.u.\(^{-1}\), respectively, as shown in Tables 2 and 3 are in good agreement with theirs.

In general, RXVSi is stabler than RXVAl in all three types of structures. Furthermore, the LuXVZ Heusler compounds are stabler than YbXVZ in all the structures. The stabllest case among all listed in Table 1 is that of LuCoVSi in the type III structure with the largest cohesive energy of 20.12 (eV f.u.\(^{-1}\)), whereas type III YbFeVAl is the most unstable with the smallest cohesive energy of 13.69 (eV f.u.\(^{-1}\)).

Finally, for all alloys in all structures except type II YbNIVSi and YbNiVSi, RNIVZ has the largest equilibrium lattice constant.

As for the cohesive energies (equivalently the structure stability) of the RXVZ Heusler compounds listed in Table 1, in general, RXVSi is stabler than RXVAl in all three types of structures. Furthermore, the LuXVZ Heusler compounds are stabler than YbXVZ in all the structures. The stabllest case among all listed in Table 1 is that of LuCoVSi in the type III structure with the largest cohesive energy of 20.12 (eV f.u.\(^{-1}\)), whereas type III YbFeVAl is the most unstable with the smallest cohesive energy of 13.69 (eV f.u.\(^{-1}\)).


Table 3 Calculated magnetic ground state, total spin magnetization ($m_t$), atomic spin magnetization ($m_x$, $m_y$, and $m_z$) for R, X, and Z atom, respectively, magnetization energy ($E_m = E_{FM} - E_{AHM}$), and the total magnetization ($M_t$) obtained using the Slater–Pauling rule. FM, FiM, HM, AHM, and MSC are ferromagnetic metal, ferrimagnetic metal, half-metal, antiferromagnetic half-metal, and magnetic semiconductor, respectively.

| RXVZ | Magnetic state | $m_x$ | $m_y$ | $m_z$ | $E_m$ (eV f.u.$^{-1}$) | $M_t$ |
|------|----------------|-------|-------|-------|------------------------|-------|
|      | Type I         |       |       |       |                        |       |
| YbFeVAl | FM            | 0.06  | -0.11 | 2.16  | -1.85                  | 0.023 | -0.141 |
| YbCoVAl | HM            | 1.00  | 0.06  | -0.87 | 1.68                   | -0.066 | -0.194 |
| YbNiVSi | FM            | 2.11  | 0.07  | -0.09 | 2.09                   | -0.115 | -0.518 |
| YbFeVSi | HM            | 1.00  | 0.13  | -1.49 | 2.03                   | -0.008 | -0.215 |
| YbCoVSi | HM            | 2.00  | 0.12  | -0.51 | 2.12                   | -0.046 | -0.340 |
| YbNiVSi | HM            | 3.00  | 0.15  | 0.16  | 2.42                   | -0.070 | -0.773 |
| LuFeVAl | NM            | 0.00  |       |       |                        |       |
| LuCoVAl | HM            | 2.00  | 0.30  | -0.40 | 1.87                   | -0.037 | -0.310 |
| LuNiVSi | FM            | 3.04  | 0.34  | 0.23  | 2.23                   | -0.058 | -0.698 |
| LuFeVSi | HM            | 2.00  | 0.38  | -0.48 | 1.80                   | 0.003  | -0.316 |
| LuCoVSi | HM            | 3.00  | 0.37  | 0.50  | 1.93                   | -0.025 | -0.399 |
| LuNiVSi | FM            | 3.99  | 0.50  | 0.57  | 2.47                   | -0.070 | -0.720 |
|      | Type II        |       |       |       |                        |       |
| YbFeVAl | AHM           | 0.00  | -0.04 | 2.56  | -2.07                 | -0.012 | -0.565 |
| YbCoVAl | FM            | 2.82  | -0.03 | 0.99  | 1.64                   | -0.001 | -0.171 |
| YbNiVSi | FM            | 2.91  | 0.02  | 0.32  | 2.15                   | 0.043  | -0.440 |
| YbFeVSi | FM            | 0.58  | -0.02 | 2.62  | -1.87                 | 0.133  | -0.703 |
| YbCoVSi | FM            | 2.99  | -0.02 | 1.19  | 1.59                   | 0.013  | -0.313 |
| YbNiVSi | FM            | 2.27  | 0.01  | 0.19  | 1.87                   | -0.049 | -0.431 |
| YbCoVSi | FM            | 1.43  | -0.07 | 0.33  | 1.11                   | -0.018 | -0.056 |
| LuFeVAl | FM            | 2.98  | -0.07 | 1.22  | 1.64                   | 0.026  | -0.366 |
| LuNiVSi | FM            | 2.50  | -0.04 | 0.33  | 1.97                   | 0.003  | -0.439 |
| LuFeVSi | FM            | 1.82  | 0.01  | 2.34  | -0.53                 | 0.067  | -0.455 |
| LuCoVSi | FM            | 2.96  | -0.03 | 1.26  | 1.53                   | 0.030  | -0.349 |
| LuNiVSi | FM            | 2.43  | 0.05  | 0.19  | 1.93                   | -0.056 | -0.294 |

| RXVZ | Magnetic state | $m_x$ | $m_y$ | $m_z$ | $E_m$ (eV f.u.$^{-1}$) | $M_t$ |
|------|----------------|-------|-------|-------|------------------------|-------|
|      | Type III       |       |       |       |                        |       |
| YbFeVAl | FM            | 1.72  | -0.06 | 2.06  | -0.17                 | -0.037 | -0.131 |
| YbCoVAl | FM            | 1.80  | 0.10  | -0.53 | 2.05                   | -0.015 | -0.417 |
| YbNiVSi | FM            | 2.33  | 0.08  | -0.10 | 2.20                   | -0.052 | -0.651 |
| YbFeVSi | FM            | 1.00  | 0.24  | -1.82 | 2.29                   | -0.009 | -0.400 |
| YbCoVSi | FM            | 2.12  | 0.12  | -0.16 | 2.02                   | -0.047 | -0.415 |
| YbNiVSi | FM            | 3.00  | 0.26  | -0.03 | 2.48                   | -0.042 | -0.559 |
| LuFeVAl | FM            | 2.83  | 0.11  | 0.77  | 1.78                  | -0.031 | -0.230 |
| LuCoVAl | FM            | 2.20  | 0.15  | -0.24 | 2.10                   | -0.025 | -0.581 |
| LuNiVSi | FM            | 3.00  | 0.23  | -0.01 | 2.42                   | -0.013 | -0.834 |
| LuFeVSi | FM            | 2.00  | 0.27  | -0.73 | 2.15                   | -0.002 | -0.412 |
| LuCoVSi | MSC           | 3.00  | 0.26  | 0.06  | 2.34                   | -0.011 | -0.656 |
| LuNiVSi | FM            | 3.70  | 0.35  | 0.32  | 2.56                   | 0.002  | -0.432 |

$M_t = Z_t - 24$ as listed in Table 2 where $Z_t$ is the total number of valence electrons and $M_t$ is the total spin magnetic moment in the unit cell. As shown in the table, the calculated magnetic moments somewhat follow the trend given by the Slater and Pauling rule.

The magnetization energy listed in Table 3 is the energy required to magnetize materials. The negative values for all the studied compounds therefore indicate the stability of the magnetic ground state in these materials. The magnetization energy is not only proportional to the total spin magnetization but also the spin configuration and the crystal structure. For example, in type I the total spin magnetization is 1.00, 2.00, and 3.00 ($\mu_B$ f.u.$^{-1}$) for YbFeVSi, YbCoVSi, and YbNiVSi, respectively, whereas their magnetization energies are $-0.215$, $-0.340$ and $-0.773$ (eV f.u.$^{-1}$). The total spin magnetization of type II YbFeVAl is zero; however, the magnetization energy is $-0.565$ (eV f.u.$^{-1}$). This is because of the large magnitude of atomic spin moments, though the total magnetization is zero.

Table 3 indicates that most of the RXVZ Heusler alloys with the type I structure are in the ferromagnetic half-metallic ground state, whereas a few of them are in the ferrimagnetic, ferromagnetic, and non-magnetic metallic ground states. Fig. 2 shows the half-metallic band structure (BS) and density of states (DOS) of LuFeVSi, LuCoVSi, and LuCoVAl EQH compounds in the type I structure. They all have similar electronic structures with a conducting band in the spin up channel and an insulating band gap in the spin down channel at the Fermi level ($E_f$), leading to the half-metallic behavior with 100% spin polarized carriers at $E_f$. In particular, owing to the same number of valence electrons, LuFeVSi (Fig. 2(a and b)) and LuCoVAl (Fig. 2(e and f)) show more or less the same BS and DOS with $E_f$ located at nearly the same

Fig. 2 Band structures (left panels) and density of states (right panels) of LuFeVSi, LuCoVSi, and LuCoVAl EQH compounds in the type I structure. These Heusler compounds are all half-metals. The Fermi level is shifted to zero as the reference.
position and having the same integer magnetic moment of 2 $\mu_B$ (Table 3) while in LuCoVSi (Fig. 2(c and d)), with one additional electron filled in the spin up d-band, the Fermi level hence locates at a higher position with a larger integer magnetic moment of 3 $\mu_B$ (Table 3). The energy band gap at $E_f$ in LuFeVSi, LuCoVSi, and LuCoVAl are respectively 0.5, 0.5, and 0.3 eV in the spin minority states. The smaller gap in LuCoVAl is presumably due to the strong metallic character of Al with more dispersive bands. Besides, they all exhibit an indirect band gap in the minority spin channel. On the other hand, the BS and DOS of type 1 YbFeVAl in the ferrimagnetic (FiM) metal, YbNiVAl in the ferromagnetic (FM) metal, and LuFeVAl in the non-magnetic (NM) metal ground states are plotted in Fig. 3 for a comparison with the half-metallic (HM) electronic structures in Fig. 2.

As shown in Table 3, RXVZ Heusler alloys in type II and III structures result in several interesting magnetic ground states. For example, type II YbFeVAl belongs to the rare category of an antiferromagnetic half-metal (AHM) with zero magnetic magnetization, and type III LuCoVSi turns out to be an unusual magnetic semiconductor (MSC) with an integer magnetic moment of 3 $\mu_B$. The band structures (BS) and density of states (DOS) of these interesting magnetic phases together with those of a typical half-metallic type III LuFeVSi are depicted in Fig. 4 for comparison. For type II YbFeVAl (Fig. 4(a and b)), the spin up channel is conducting while the spin down channel is insulating. The atom-decomposed DOS (Fig. 4(b)) demonstrates that Fe bands (red) are mainly in the majority spin whereas the V bands (green) are mainly in the minority spin, resulting in the AHM magnetic ground state. Such an intriguing electronic structure gives rise to a spin polarized transport behavior with the overall system remaining nonmagnetic, which is of high potential in future spintronic devices. There exists a direct energy band gap of 0.3 eV at the Fermi level in the minority spin channel (Fig. 4(a)). Note that this is the only direct band gap of 0.3 eV at the Fermi level in the minority spin channel (Fig. 4(a)). Note that this is the only direct band gap of 0.3 eV at the Fermi level in the minority spin channel (Fig. 4(a)).

Fig. 3 Band structures (left panels) and density of states (right panels) of YbFeVAl-FiM, YbNiVAl-FM, LuFeVAl-NM phases in the type I structure. The Fermi level is shifted to zero as the reference.

Fig. 4 Band structures (left panels) and density of states (right panels) of type II YbFeVAl in the antiferromagnetic half-metallic (AHM), type III LuFeVSi in the ferromagnetic half-metal (HM), and type III LuCoVSi in the magnetic semiconductor (MSC) ground state. The Fermi level is shifted to zero as the reference.
gap found in the minority spin among all the half-metallic cases studied in this work. All the other half-metals exhibit indirect band gaps similar to that of type III LuFeVSi in Fig. 4(c and d). As shown in the density of states in Fig. 2 and 4, Lu bands are relatively narrower than those of Yb. This is presumably due to the nearly closed shell electronic configuration of Lu with a relatively small orbital size and localized behavior. Consequently, the band dispersion is suppressed with a smaller bandwidth. Finally, Fig. 4(e and f) show that the type III LuCoVSi EQH compound is a magnetic semiconductor with an indirect band gap of 0.2 eV. Such a magnetic semiconductor ground state is very rare while of high importance in spintronics. We hope that this newly predicted magnetic semiconductor can be synthesized and applied for spintronic devices in the near future.

B Mechanical properties

To understand the mechanical properties and stability of a solid, we have calculated the elastic constants and related physical quantities of the rare-earth Heusler compounds RXVZ as discussed below. Since the EQH compounds studied in this work all have the cubic symmetry, we need only to consider three independent elastic constants, i.e., $C_{11}$, $C_{12}$, and $C_{44}$. These independent elastic constants are determined by performing certain finite distortions of the lattice and calculating the elastic constants from the strain–stress relations. Once the elastic constants are obtained, we can determine the bulk modulus $B$, shear modulus $G$, Voigt shear modulus $G_V$, and Reuss shear modulus $G_R$.

\[ G = \frac{G_R + G_V}{2} \]

\[ G_V = \frac{C_{11} - C_{12} + 3C_{44}}{5} \]

\[ G_R = \frac{5(C_{11} - C_{12})C_{44}}{4C_{44} + 3(C_{11} - C_{12})} \]

\[ B = \frac{C_{11} + 2C_{12}}{3} \]

where $G_V$ and $G_R$ are derived using different approaches. The $G_V$ is based on the assumption of uniform local strain, while the $G_R$ is based on the assumption of uniform local stress. These two different approaches have been shown to yield the strict upper and lower bounds, respectively. Therefore, the average value of the $G_V$ and $G_R$ is usually used.

The mechanical stability criteria for the cubic structure are as follows:

\[ C_{44} > 0, \]

\[ C_{12} < B < C_{11}, \]

\[ B > 0. \]

As shown in Table 4, all the calculated $C_{44}$ and $B$ coefficients are positive. Consequently, the mechanical stability will be determined by eqn (9) or equivalently the sign of the anisotropy factor $A$ in eqn (6). If the calculated coefficient $A$ is negative, which indicates the violation of eqn (9), the structure is thus unstable. As can be seen in the table, most of the studied cases are mechanically stable except that YbNiVSi, LuNiVAl, LuCoVSi, and LuNiVSi in the type I structure, and YbNiVSi in the type II structure are mechanically unstable because of their negative value of the anisotropy factor $A$. In principle, the negative modules listed in Table 4 are related to the violation of eqn (9), in which $C_{11} - C_{12}$ can be understood as the elastic constant under the orthogonal distortion of the conserving volume. In addition to the anisotropy factor $A$, the instability of these unstable EQH compounds is also shown through the Reuss shear modulus $G_R$. In addition, for type I YbNiVSi, the unstable features can further be found in the Hill shear modulus $G$ and Young’s modulus $E$ as well. Apart from this, the remaining EQH compounds are all mechanically stable. Note that all EQH compounds in type III structure are stable, indicating that type III structure provides robust mechanical stability for the rare-earth Heusler compounds RXVZ.

Generally, the Young’s modulus $E$ can present the stiffness of the material: a higher value of $E$ indicates that the material is stiffer. As shown in Table 4, most of the $E$ values are large. However it is very small for type I LuCoVSi (4.2 GPa), LuNiVSi (7.9 GPa), and YbNiVSi (~25.2 GPa). These low or even negative Young’s modulus values $E$ imply that these EQH compounds are very soft and tend to be mechanically unstable. In general, EQH alloys in the type III structure exhibit higher values of $E$, whereas the type I structure leads to lower $E$ values. As a result, the general order of stiffness is type III > type II > type I.

The well known Pugh’s ratio of $B/G$ can be used to estimate the failure behavior of compounds. A material is classified to be ductile if $B/G > 1.75$, otherwise it is considered to be brittle. According to this empirical criterion, all type I and II EQH compounds except type I YbFeVAl, YbCoVAl, and YbFeVSi are ductile in nature. On the contrary, all EQH compounds in type III are brittle materials, except YbFeVAl, LuFeVAl, and LuNiVSi. This result is consistent with the trend of stiffness. In other words, the more stiff the material, the less ductile it is.

The Poisson’s ratio provides useful information to understand the characteristics of the bonding forces in a material. It has been proved that $\nu = 0.25$ is the lower limit of the central force solid, and $\nu = 0.5$ is the upper limit of the infinite elastic anisotropy. It has also been suggested that brittleness and ductility can be judged considering the values $\nu < 1/3$ and $\nu > 1/3$, respectively. According to the above conditions, we can find that type I EQH compounds all show ductile behavior, except for YbFeVAl, YbCoVAl, and
The anisotropy factor \( A \), as shown in Table 4 of a solid can be used to predict whether the considered EQH compounds show mechanical anisotropy. \( A \), also called the shear anisotropy factor, is defined as the ratio of the shear modulus between [001] and [1−10] directional stress on the shear plane (110). For an orthorhombic crystal, the shear modulus for a shear system \( \kappa_{hkl}\parallel\{110\} \) is given by42,43

\[
\frac{1}{G} = 4s_{11}(l_{11}t_{11}^2 + l_{12}t_{12}^2 + l_{13}t_{13}^2)
+ 8s_{12}(l_{11}t_{12}t_{12} + l_{12}t_{12}t_{22} + l_{13}t_{13}t_{22} + 2l_{11}t_{13}t_{13})
+ s_{44}(l_{11}t_{12} + l_{12}t_{12} + l_{13}t_{13})^2 + (l_{12}t_{12} + l_{11}t_{11} + l_{13}t_{13})^2,
\]

where \((l_{11}, l_{12}, l_{13})\) is the direction of the shear stress, \((l_{21}, l_{22}, l_{23})\) is the normal vector to the shear plane \((hk\ell)\), and \(s_{ij}\) are the elastic compliance constants \((s = C_{ij}^{-1})\). Also, the Young’s modulus depends on the stress direction \((l_{1}, l_{2}, l_{3})\). The relation between them is42,43

\[
\frac{1}{E} = s_{11}l_{11}^4 + s_{12}l_{12}^4 + s_{13}l_{13}^4 + (2s_{12} + s_{66})l_{11}^2l_{22}^2
+ (2s_{23} + s_{44})l_{22}^2l_{33}^2 + (2s_{13} + s_{55})l_{11}^2l_{33}^2.
\]

Therefore, the elastic anisotropy factor can be defined not only by the shear modulus but also by the bulk and Young’s moduli. Moreover, there are other definitions of elastic anisotropy factors such as percentage anisotropy incompressibility and shear44 anisotropy. The shear anisotropic factors provide a measure of the degree of anisotropy in the bonding between atoms in different planes. As shown in Table 4, the value of \( A \) for all the studied EQH compounds is not equal to 1, which...
indicates that they are all elastic anisotropic. The difference of $A$ from 1 (either larger or smaller than 1) provides an indication to estimate the level of elastic anisotropy acquired by the crystals.

To clarify the elastic anisotropy, we also present the orientation dependence of the shear modulus and Young’s modulus as shown in Fig. 5 and 6, respectively. Fig. 5 shows the shear modulus corresponding to all directions on the (110) shear plane. It is clear that Fig. 5(b), (c), (f), and (i) show a complex cusp pattern for the type I structure and Fig. 5(i) for the type II structure, which means that these compounds are not stable. In addition, it can also be seen that the shear modulus show significant anisotropy. Indeed, the shear moduli $G(100)[001]$ and $G(100)[110]$ are equivalent to $C_{44}$ and $(C_{11} - C_{12})/2$, respectively. This indicates that $A$ is the ratio between the $x$-intercept and the $y$-intercept. Further, Fig. 5 also illustrates a general trend that the anisotropic levels of type III EQH compounds are lower than those of type I and type II. On the other hand, Fig. 6 shows the Young’s modulus with the tensile axis rotated from [100] to [010]. Similar to the shear modulus shown in Fig. 5, the Young’s modulus [Fig. 6] also shows that all EQH compounds in the type III structure are more isotropic than those in type I and II structures.

Piezoelectricity states that a material can generate electric dipole moments under external stress. This process can be reversed to produce stress on a material by applying an external electric field. For materials with the cubic symmetry, the piezoelectric tensor $e_{ij}$ can be reduced to

$$e_{ij} = \begin{pmatrix} 0 & 0 & 0 & e_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & e_{14} & 0 \\ 0 & 0 & 0 & 0 & 0 & e_{14} \end{pmatrix}. \quad (13)$$

The calculated piezoelectric constant $e_{14}$ is listed in Table 4 as $e$ (C m$^{-2}$). We found that for most of the studied rare earth EQH compounds, the piezoelectric constant $|e|$ is small, usually less than 1 (C m$^{-2}$). The commonly used piezoelectric material, lead zirconate titanate, exhibits a maximum value of piezoelectric tensor components in the range from 6 to 12 (C m$^{-2}$).45 In general, materials with $|e| > 3$ might be useful for piezoelectrics. Over the 36 cases studied in this work, only one, i.e., type II LuNiVSi, exhibits an applicable piezoelectric constant of 7.192 C m$^{-2}$. 

Fig. 5 Contours of the shear modulus ($G$, in GPa) for shear stress along [001] to [1-10] on the (110) shear plane.
IV. Conclusions

We have systematically studied the rare earth equiatomic quaternary Heusler compounds through first-principles calculations based on density functional theory. Twelve EQH compounds in three types of structures are considered. Most of the rare earth EQH compounds show magnetic ground states. 7 out of 12 EQH compounds in the type I structure are ferromagnetic half-metals with integer magnetic moments. Type II YbFeVAl is found to be the rare antiferromagnetic half-metal with zero total spin moment. Moreover, type III LuCoVSi is found to be an unusual magnetic semiconductor to have an integer magnetic moment of 3.00 $\mu_B$ and an indirect band gap of 0.2 eV. Both AHM and MSC phases are difficult to find but are of high potential in future spintronic devices. Structural and magnetic stability related factors formation energy, magnetization energy, as well as mechanical stability related factors such as the bulk, shear, and Young's modulus, and the Poisson's and Pugh's ratios of these EQH compounds are presented. Our work provides guidelines on the synthesis of useful materials for future spintronic devices.

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgements

This work was supported by China Medical University, Taiwan (CMU108-N-25) and the Ministry of Science and Technology, Taiwan (MOST-107-2112-M-039-002-MY2, MOST-106-2112-M-007-012-MY3). The authors are also thankful for the support from the Academia Sinica, NCHC, CINC-NTU, AS-iMATE-109-13, and CQT-NTHU-MOE, Taiwan.

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