First-principles prediction of half-Heusler half-metals above room temperature

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Half-metallicity (HM) offers great potential for engineering spintronic applications, yet only few magnetic materials present metallicity in just one spin channel. In addition, most HM systems become magnetically disordered at temperatures well below ambient conditions, which further hinders the development of spin-based electronic devices. Here, we use first-principles methods based on density functional theory (DFT) to investigate the electronic, magnetic, structural, mixing, and vibrational properties of 90 XYZ half-Heusler (HH) alloys (X = Li, Na, K, Rb, Cs; Y = V, Nb, Ta; Z = Si, Ge, Sn, S, Se, Te). We disclose a total of 28 new HH compounds that are ferromagnetic, vibrationally stable, and HM, with semiconductor band gaps in the range of 1–4 eV and HM band gaps of 0.2–0.8 eV. By performing Monte Carlo simulations of a spin Heisenberg model fitted to DFT energies, we estimate the Curie temperature, TC, of each HM compound. We find that 17 HH HM remain magnetically ordered at and above room temperature, namely, 300 ≤ TC ≤ 450 K, with total magnetic moments of 2 and 4 µB. A further materials sieve based on zero-temperature mixing energies let us to conclude 5 overall promising ferromagnetic HH HM at and above room temperature: NaVsSi, RbVTe, CsVS, CsVSe, and RbNbTe. We also predict 2 ferromagnetic materials that are semiconductor and magnetically ordered at ambient conditions: LiVSi and LiVGe.

I. INTRODUCTION

Half-metals (HM) with full spin polarization at the Fermi level are of great potential for spintronic applications [1, 2]. In particular, HM are considered to be ideal for injecting spin-polarized currents into semiconductors [3, 4] and for manufacturing electrodes for magnetic tunnel junctions and giant magnetoresistance devices [5, 6]. Half-Heusler (HH) alloys comprise a relatively large family of multifunctional materials with chemical formula XYZ and cubic symmetry (space group Fm3m); the archetypal HH compound NiMnSb was the first half-metal material to be ever reported [7]. The structural compatibility of HH HM with typical cubic semiconductors, the potential huge number of current HH HM compounds [8], and the possibility of combining different HH to form HM layered structures [9], open great prospects in the field of spin-based electronics.

In recent years, HH alloys have been studied extensively with computational first-principles methods [10, 11]. The structural simplicity, rich variety, and predictable electronic behaviour (e.g., modified Slater-Pauling rule [12]) of HH alloys convert these materials into a perfect target for automated computational searches of HM [13,14]. The structural stability and magnetic properties of HH calculated at zero temperature are the usual materials descriptors employed to guide the theoretical searches of candidate HM. However, analysis of the corresponding magnetic properties at room temperature, which are crucial for the engineering of practical applications [15, 16], usually are neglected due to the large computational load associated with first-principles simulation of thermal effects [15]. Furthermore, ferromagnetic (FM) spin ordering is widely assumed in such computational investigations [19, 20] regardless of the fact that anti-ferromagnetic (AFM) spin ordering is also possible in HM materials [12, 21, 22]. In order to provide improved guidance to future experiments, it is convenient then to examine the magnetic properties of HH HM at T ̸= 0 K conditions, along with their vibrational and mixing stabilities.

In this article, we investigate the electronic, magnetic, structural, mixing, and vibrational properties of 90 XYZ HH alloys (X = Li, Na, K, Rb, Cs; Y = V, Nb, Ta; Z = Si, Ge, Sn, S, Se, Te) with first-principles methods based on density functional theory (DFT). Our selection of materials has been motivated by recent encouraging results reported by other authors for some similar systems [12, 24, 25]. We introduce a simple HH spin Heisenberg model fitted to FM and AFM DFT energies that allows for fast and systematic monitoring of the magnetization as a function of temperature. We predict that a total of 17 HH HM are vibrationally stable and remain magnetically ordered at and above room temperature, with total magnetic moments of 2 and 4 µB and semiconductor (half-metal) band gaps in the range of 1–4 (0.2–0.8) eV. A further materials sieve based on zero-temperature mixing energies allows us to identify 5 HH HM that are most promising for electronic applications. Meanwhile, a total of 21 HH alloys are found to exhibit an anti-ferromagnetic ground state but all of them turn out to be metallic. We also predict 2 new semiconductor FM materials that possess high thermodynamic stability and Curie temperatures. General structural, thermodynamic, and functional trends are identified across the X, Y, and Z series. Hence, our computational study discloses a number of electronic materials and design strategies that should be useful for spintronic applications.
II. METHODS

In what follows, we explain the technical details of our first-principles calculations. We also describe the simple spin Heisenberg model that we have devised to analyse the magnetic properties of HH alloys at finite temperatures, along with the technical details of the accompanying Monte Carlo simulations.

A. First-principles calculations

Density functional theory (DFT) calculations have been performed with the self-consistent full potential linearized augmented plane wave (FP-LAPW) method, as implemented in the WIEN2K code [26]. The generalised gradient approximation to the exchange-correlation energy due to Perdew-Burke-Ernzerhof (PBE) [27] has been employed in this study to estimate energies and determine equilibrium geometries. The value of the R_{mt} × K_{max} product, where R_{mt} is the value of the muffin-tin sphere radii and K_{max} of the plane wave cut-off energy, was fixed to 9 in order to provide highly converged results. Likewise, a dense k-point mesh of 21 × 21 × 21 was used for integrations within the first Brillouin zone (IBZ). The self-consistent threshold values adopted for the calculation of energies and equilibrium geometries were 10^{-5} eV and 10^{-4} eV/Å, respectively. In order to estimate accurate electronic and magnetic properties (e.g., band gaps and magnetic moments) at reasonable computational cost, we employed the Tran-Blaha modified Becke-Johnson (TB-mBJ) meta-GGA exchange-correlation functional [28] over the equilibrium structures generated with PBE.

The pseudopotential plane-wave DFT code VASP [29] has been also used for determining the energy difference between FM and AFM spin orderings, and for estimating vibrational lattice phonons. We used the projector-augmented wave method to represent the ionic cores [30], considering the following electrons as valence states: X s, p, and d; Y s, p, and d; and Z s and p. Wave functions were represented in a plane-wave basis truncated at 650 eV and for integrations within the IBZ we employed a dense Γ-centered k-point mesh of 16 × 16 × 16. The calculation of phonon frequencies was performed with the small displacement method [31] and the PHONOPY code [32]. The following parameters provided sufficiently well converged phonon frequencies: 190-atom supercells (i.e., 4 × 4 × 4 replication of the conventional HH unit cell) and atomic displacements of 0.02 Å.

B. Spin Heisenberg model and Monte Carlo simulations

To analyse the effects of temperature on the magnetic properties of HH alloys, we define the following spin Heisenberg Hamiltonian:

\[ E_{\text{spin}} = E_0 + \frac{1}{2} \sum_{ij} J_{ij} S_i S_j, \]  

(1)

where \( E_0 \) is a reference energy, \( S_i \) represent the magnetic moment of ion \( i \), and \( J_{ij} \) the exchange interactions of ion \( i \) with the rest. In our model, we only consider spin couplings between nearest magnetic ions (which add up to 12, given that the symmetry of the magnetic sublattice is face centered cubic) and assume that all exchange interactions are equal. Based on such simplifications, the value of the model parameters can be calculated straight-
forwardly with DFT methods as:

\[ E_0 = \frac{1}{2} (E_{\text{FM}} + E_{\text{AFM}}) \]

\[ J_{ij} = \frac{1}{8|S|^2} (E_{\text{FM}} - E_{\text{AFM}}), \]

where \( E_{\text{FM}} \) and \( E_{\text{AFM}} \) are the energy of the crystal considering perfect ferromagnetic and anti-ferromagnetic spin arrangements, respectively. (We recall that in the AFM spin configuration each magnetic ion sees 8 out of its 12 nearest neighbors with opposite spin orientation \[36\].) It is worth noting that in spite of the simplicity of the adopted spin Heisenberg Hamiltonian, similar models have been able to provide accurate results for the \( T \)-dependence of the magnetization of complex magnetic materials (e.g., multiferroic oxide perovskites \[33-35\]).

Classical Monte Carlo (MC) simulations of the spin Heisenberg Hamiltonian just explained were performed to estimate the magnetization of HH alloys (that is, equal to the sum of all indvidual spins) as a function of temperature. We used a periodically-repeated simulation box containing \(20 \times 20 \times 20\) spins. Thermal averages were computed from runs of 50,000 MC sweeps performed after equilibration (which consisted of the same number of MC steps). A small symmetry-breaking magnetic anisotropy was introduced in the MC simulations to facilitate the accompanying numerical analysis \[37\]. By using this setup and monitoring the evolution of the magnetization as a function of \( T \), we were able to estimate magnetic transition temperatures, \( T_C \), with a numerical accuracy of 25 K.

III. RESULTS AND DISCUSSION

We start this section by providing an overview of the computational strategy that we have followed to determine the ground-state configurations of HH alloys, and the general classification that results from our calculations based on their structural, electronic, and magnetic properties. Then, we explain in detail the electronic and vibrational properties of the disclosed HH HM, followed by a discussion on their magnetic phase transition temperatures and zero-temperature mixing energies. Finally, we highlight the HH alloys that according to our calculations are most promising for spintronics applications.

A. Overview of the 90 \(XYZ\) HH alloys

The \(XYZ\) HH alloys considered in this study feature an alkali metal in the \(X\) position (Li, Na, K, Rb, and Cs), a transition metal in the \(Y\) position (V, Nb, and Ta), and a non-metal \(sp\)-element in the \(Z\) position (Si, Ge, Sn, S, Se, and Te). The cubic HH unit cell consists of three interpenetrating face centered cubic (fcc) sublattices that together render a crystal structure with \(F\overline{4}3m\) symmetry. There exist three possible atomic arrangements compatible with this structure, namely, \(T1\), \(T2\), and \(T3\), which are generated by exchanging the Wyckoff positions of the \(X\), \(Y\), and \(Z\) ions (see Fig. 1). The physical properties of HH alloys may be greatly influenced by their specific atomic arrangement \[16\], hence configurations \(T1\), \(T2\), and \(T3\) need to be all considered when performing thorough functionality searches within this family of materials.

Systematic fixed-volume geometry optimizations have been carried out for each HH compound to determine the energetically most favorable atomic arrangement, equilibrium volume, and magnetic ordering. First, the equilibrium volume of each possible structure considering FM spin ordering is obtained by fitting the series of calculated energy points to a Birch-Murnaghan equation of state \[38\]; subsequently, the energy associated with AFM spin ordering is analyzed for the lowest-energy atomic arrangement obtained in the FM case. Figures 2a-b illustrate such a computational procedure for the particular case of NaVTe, which turns out to exhibit a \(T1\)-FM ground state and an equilibrium volume of 320 \(\text{Å}^3\). Once the optimal atomic arrangement, equilibrium volume, and magnetic ordering have been determined at the PBE level, we accurately calculate the corresponding...
Figure 3 shows a general classification of the 90 HH compounds analyzed in this study made on basis to their structural, magnetic, and electronic properties. A total of 56 materials present lowest energy on the T1 arrangement, 32 on the T3, and only 2 on the T2. Compounds with a light-weight alkali metal in the X position (e.g., Li, Na, and K) tend to be more stable in the T1 arrangement, whereas those with heavy-weight alkali metals (e.g., Rb and Cs) in the T3. On the other hand, compounds with a heavy-weight transition metal in the Y position (e.g., Nb and Ta) mostly are stabilized in the T1 configuration, made the exception of the HH alloys containing Cs which always adopt the T3 arrangement. Meanwhile, the role of the non-metal element occupying the Z position on
choosing the most favorable structure appears to be negligible. We note that the two compounds that adopt the T2 configuration turn out to be metallic (i.e., LiTaSn and LiNbSn); thereby, the T2 arrangement will be ignored for the remainder of the article.

At zero-temperature conditions, we find that 55 HH alloys are FM, 21 AFM, and 14 non-magnetic (see Fig.3). A total of 39 FM compounds are found to be half-metallic, 2 FM semiconductor (SC), and the rest metallic. In what follows, we describe with detail the electronic, vibrational, magnetic, and mixing properties of the 41 new HM and SC compounds that have been determined in our investigation, all of which present FM spin ordering.

B. Electronic and vibrational properties

Figure 4 shows the energy and half-metallic band gaps, $E_{BG}$ and $E_{HM}$, estimated for the 90 XYZ HH alloys considered in this study. $E_{BG}$ is the energy difference between the top of the valence band and bottom of the conduction band in the semiconductor spin channel, and $E_{HM}$ the minimum energy that an electron requires to surpass the spin gap (see Fig.5 where we represent those quantities for CsVSe). One can observe a certain correlation between these two quantities, namely, large $E_{BG}$’s are accompanied by large $E_{HM}$’s. For instance, RbNbS (T1 arrangement) has an energy band gap of 5.08 eV and HM band gap of 1.46 eV, while CsVSn (T3 arrangement) has 1.30 eV and 0.18 eV, respectively. Nevertheless, there are few compounds that in spite of having a relatively small energy band gap exhibit a relatively large HM band gap (e.g., RbNbSi in the T3 configuration for which we estimate $E_{BG} = 1.24$ eV and $E_{HM} = 0.57$ eV).

The color code employed in Fig.4 shows that the HH alloys consisting of heavy-weight X-ions (K, Rb, and Cs), light-weight Y-ions (V and Nb), and chalcogen elements (S, Se, and Te) in the Z position, generally possess the largest $E_{BG}$ and $E_{HM}$. By contrast, HH compounds with a light-weight (heavy-weight) alkali (transition) metal element like Li (Ta) in the X (Y) position mostly are metallic or present medium band gaps.
possesses a relatively small zero-temperature mixing energy of half-metallic band gap is 0.

energy band gap of RbVTe is 3.

spin ordering with a Curie temperature of $T_C = 375 \pm 25$ K, possesses a relatively small zero-temperature mixing energy of 0.14 eV/atom, and has a total magnetic moment of 4 $\mu_B$. The energy band gap of RbVTe is 3.73 eV and the accompanying half-metallic band gap is 0.83 eV. The electronic properties are calculated with the Tran-Blaha modified Becke-Johnson (TB-mBJ) meta-GGA exchange-correlation functional [28].

We note that when the chalcogen element (S, Se, and Te) in the Z position is substituted by a group-XIV element (Si, Ge, Sn), $E_{BG}$ and $E_{HM}$ generally undergo a significant reduction (see Fig.4). For instance, RbVSn has an energy band gap of 1.13 eV and a HM band gap of 0.20 eV. Such a band gap closure is consequence of a decrease in the energy separation between the $Z$ $p$ orbitals and $X–Y$ $d$ bonding and antibonding states (not shown here), and it occurs when the number of valence electrons in the system changes from 12 (S, Se, Te) to 10 (Si, Ge, Sn). Interestingly, the energy band gap changes as induced by $Z$-element substitutions correlate directly with changes in the magnetic moment of the ions; we will discuss in detail this and other magnetic effects in the next subsection.

Out of the 90 HH alloys investigated in this study, we have found that 39 (2) are ferromagnetic and half-metallic (magnetic semiconductor) at zero-temperature conditions. In order to provide useful guides for the experiments, is necessary also to assess the vibrational stability of the candidate materials proposed by theory. Here, we have calculated the lattice phonons for each HH alloy at the high-symmetry reciprocal point $\Gamma$, and concluded that 28 FM HM along with the 2 FM SC are vibrationally well behaved (that is, do not present imaginary phonon frequencies at the IBZ center). For some selected cases (namely, the overall most promising materials that will be discussed in Sec.III D), we have calculated also the full phonon spectrum over the entire IBZ and found that most of them are vibrationally stable (see Fig.7, where we enclose a couple of relevant examples). We have not been able to draw any robust correlation between vibrational instability and chemical structure for the HH alloys analyzed in this study. For the remainder of the article, we will focus on describing the magnetic and mixing properties of the 28 (2) FM, HM (SC), and vibrational stable compounds that we have predicted.

C. Magnetism and mixing stability

Recently, Damewood et al. [12] have proposed a modified Slater-Pauling (mSP) rule for describing the magnetic moment of the half-Heusler alloys LiMn$Z$ ($Z$ = N, P, Si). Specifically, the total magnetic moment per formula unit (expressed in units of $\mu_B$), $M$, has been parametrized as:

$$M = N_t - 8,$$  \hspace{1cm} (3)

where $N_t$ is the total number of valence electrons in the unit cell. In the present case, $N_t$ is equal to 12 for alloys displaying S, Se, or Te in the $Z$ position, and to 10 for Si, Ge, and Sn (we recall that $N_t = 1$ for the $X$ elements considered in this study, $N_t = 5$ for the $Y$’s, and $N_t = 4$ or 6 for the $Z$’s). We have found that all non-metallic and magnetic $XYZ$ alloys disclosed in this study (i.e., either HM or SC) in fact follow the mSP rule proposed by Damewood et al. [12] (some examples are provided in Table I). Interestingly, in those cases we also observe...
FIG. 7. Phonon spectrum of the semiconductor and half-metallic HH alloys LiVGe and NaVSi (both in the T1 arrangement) predicted in this study. (a) LiVGe is vibrationally stable, displays FM spin ordering with a Curie temperature of $T_C = 375 \pm 25$ K, possesses a zero-temperature mixing energy of $-0.11$ eV/atom, a total magnetic moment of 2 $\mu_B$, and an energy band gap of 1.06 eV. (b) NaVSi is vibrationally stable, displays FM spin ordering with a Curie temperature of $T_C = 300 \pm 25$ K, possesses a relatively small zero-temperature mixing energy of 0.21 eV/atom, a total magnetic moment of 2 $\mu_B$, an energy band gap of 1.11 eV, and an accompanying half-metallic band gap of 0.52 eV.

| Compound | Structure | $a_0$ (Å) | Electronic behavior | $M$ ($\mu_B$) | $E_{\text{BG}}$ (eV) | $E_{\text{HM}}$ (eV) | $T_C$ (K) | $E_{\text{mix}}$ (eV/f.u.) |
|----------|-----------|-----------|---------------------|---------------|---------------------|---------------------|----------|------------------------|
| LiVSi    | T1        | 5.85      | SC                  | 2.0           | 1.43                | –                   | 300      | -0.11                  |
| LiVGe    | T1        | 5.93      | SC                  | 2.0           | 1.06                | –                   | 375      | -0.11                  |
| NaVSi    | T1        | 6.25      | HM                  | 2.0           | 1.11                | 0.52                | 300      | +0.21                  |
| NaVTe    | T1        | 6.84      | HM                  | 4.0           | 4.18                | 0.54                | 150      | -0.12                  |
| KVSi     | T3        | 6.55      | HM                  | 2.0           | 1.49                | 0.21                | 375      | +0.56                  |
| RbVTe    | T3        | 7.27      | HM                  | 4.0           | 3.73                | 0.83                | 375      | +0.14                  |
| CsVS     | T3        | 6.93      | HM                  | 4.0           | 3.92                | 0.68                | 300      | +0.01                  |
| CsVSSe   | T3        | 7.13      | HM                  | 4.0           | 3.66                | 0.66                | 375      | +0.11                  |
| RbNbSi   | T3        | 6.77      | HM                  | 2.0           | 1.24                | 0.57                | 450      | +0.83                  |
| RbNbSn   | T3        | 7.19      | HM                  | 2.0           | 1.19                | 0.33                | 450      | +0.83                  |
| **RbNbTe** | T3    | 7.41      | HM                  | 4.0           | **3.82**            | **0.75**            | **450**  | **+0.40**              |
| CsNbSi   | T3        | 6.87      | HM                  | 2.0           | 0.47                | 0.11                | 375      | +0.91                  |
| CsNbGe   | T3        | 6.96      | HM                  | 2.0           | 0.62                | 0.14                | 375      | +0.91                  |
| CsNbSn   | T3        | 7.28      | HM                  | 2.0           | 0.69                | 0.16                | 375      | +0.94                  |
| CsNbTe   | T3        | 7.55      | HM                  | 4.0           | 3.23                | 0.39                | 450      | +0.49                  |
| KTaSn    | T1        | 7.17      | HM                  | 2.0           | 1.31                | 0.54                | 300      | +0.88                  |
| RbTaSi   | T1        | 6.89      | HM                  | 2.0           | 1.36                | 0.66                | 300      | +0.92                  |
| RbTaGe   | T1        | 6.99      | HM                  | 2.0           | 1.39                | 0.55                | 300      | +0.97                  |
| RbTaSn   | T3        | 7.16      | HM                  | 2.0           | 1.05                | 0.35                | 375      | +1.03                  |
| RbTaTe   | T3        | 7.37      | HM                  | 4.0           | 3.70                | 0.24                | 375      | +0.75                  |

TABLE I. Properties summary of the most relevant HH alloys predicted in this study considering their lowest-energy configuration. The 7 overall most promising HH compounds are highlighted in bold. All systems are vibrationally stable and display FM spin ordering. The electronic properties are calculated with the Tran-Blaha modified Becke-Johnson (TB-mBJ) meta-GGA exchange-correlation functional [28]. The numerical uncertainty in our $T_C$ results is ±25 K.
a clear correlation between the total magnetization and size of the energy band gap: large $M$’s and large $E_{BG}$’s occur simultaneously in the same compounds. From an applied point of view, this seems to be a positive finding since wide band gap HM alloys then are likely to be also magnetically robust. Nevertheless, the size of the magnetic moments does not provide any information on the variation of the magnetization at $T \neq 0$ conditions, which is related to the exchange interactions between the magnetic moments.

We have estimated the magnetic transition temperature, $T_C$, for the 28 (2) FM, HM (SC), and vibrational stable compounds determined in this study, by using the computational methods explained in Sec. II B. Our $T_C$ results are shown in Fig. 8. It is appreciated that compounds with a heavy-weight alkali metal in the X position (Rb and Cs) concentrate the highest magnetic transition temperatures (see also Table I). For instance, RbNbSn displays a Curie temperature of $450 \pm 25$ K and CsVSe of $375 \pm 25$ K, while NaVTe becomes paramagnetic at $150 \pm 25$ K and KTaGe at $225 \pm 25$ K. We ascertain the lack of any correlation between the size of the ionic magnetic moments, $M$, and the Curie temperature of the system; for example, RbNbSn displays $M = 2 \mu_B$ and $T_C = 450 \pm 25$ K while for RbNbTe we estimate $M = 4 \mu_B$ and the same magnetic transition temperature. Interestingly, we find that a total of 17 (2) FM, HM (SC), and vibrational stable compounds remain magnetically ordered at or above room temperature. All of them are listed in Table I and will be discussed in the next subsection.

Finally, we calculated the zero-temperature mixing energy, $E_{mix}$, of the 28 (2) FM, HM (SC), and vibrational stable compounds disclosed in this work, by using the formula:

$$E_{mix} = E_{mix}^{HH} - (E_{X}^{fcc} + E_{Y}^{fcc} + E_{Z}^{fcc})$$

where $E_{X}^{HH}$ represents the ground-state energy of the HH alloy, and $E_{X}^{fcc}$ the energy of the bulk A crystal considering an equilibrium fcc structure. $E_{mix}$ provides a quantitative estimation of how stable the $XYZ$ system is against decomposition into $X$-, $Y$-, and $Z$-rich regions. In particular, negative (positive) values of the mixing energy indicate high (low) stability of the compound against phase decomposition. We should note, however, that the configurational entropy of the HH alloy, which is totally neglected in Eq. (4), will always contribute favourably to the free energy and enhance the chemical stability of the $XYZ$ compound at finite temperatures [39, 40]. Consequently, a positive but small value of $E_{mix}$ does not necessarily imply phase separation under realistic $T \neq 0$ K conditions. Here, we (somewhat arbitrarily) consider that a $E_{mix}$ threshold value of 0.2 eV per formula unit can be used to sieve materials with reasonably good mixing stability from those with tendency for phase separation [41].

Figure 9 shows our $E_{mix}$ results; only 7 compounds out of 30 (i.e., 28 HM and 2 SC) display zero-temperature mixing energies below 0.2 eV per formula unit. We note that all of those low mixing energy compounds contain V in the Y position, namely, LiVSi (SC), LiVGe (SC), NaVTe (HM), NaVSi (HM), RbVTe (HM), CsVS (HM), and CsVSe (HM) (see Table I). Specifically, only the first three alloys listed above present negative $E_{mix}$ values, while for CsVS we obtain a practically null mixing energy. On the other hand, KVSi (HM), RbNbTe (HM), and CsNbTe (HM) exhibit mixing energies close to 0.50 eV/f.u., and for the rest of compounds we estimate $E_{mix}$’s that are close to 1.00 eV per formula unit. These results indicate that most of the HH HM reported in this work, in spite of possessing relatively high Curie...
temperatures, are likely to present phase separation issues, which is not desirable for practical applications.

Meanwhile, we observe that when the element occupying the Z position in the HH alloy is a chalcogen (S, Se, and Te) the resulting mixing energy is noticeably smaller than when the element belongs to group-XIV of the periodic table (Si, Ge, Sn). For instance, we find that $E_{\text{mix}}$ amounts to $-0.12$ eV/f.u. for NaVTe and to 0.21 eV/f.u. for NaVSi (see Table I). The same behaviour is observed also for other compounds presenting either Nb or Ta in the Y position (e.g., for RbTaSn we estimate 1.03 eV/f.u. and for RbTaTe 0.75 eV/f.u.). Therefore, a possible strategy for improving the mixing stability of some of the new HH HM compounds reported in this study (e.g., KVSi with $E_{\text{mix}} = 0.56$ eV/f.u. and RbNiSi with $E_{\text{mix}} = 0.83$ eV/f.u.) may consist in doping with light-weight alkali metals (Li and Na) in the X position (although this may also lead to some unwanted increase in the energy band gap and Curie temperature of the alloy, see present and previous sections) and with chalcogen species in the Z position.

D. Most promising magnetic HH alloys

Table I shows the 19 vibrationally stable and ferromagnetic compounds predicted in this study that possess a Curie temperature equal or above room temperature. Two out of those 19 alloys are semiconductor while the rest are half-metallic. We have also included NaVTe in the table, in spite of presenting a relatively low Curie temperature of 150 K, owing to its good mixing stability properties ($E_{\text{mix}} = -0.12$ eV/f.u.). From an applied perspective, an overall promising HM (or magnetic semiconductor) material should present the following qualities: (1) being vibrationally and chemically stable, (2) high Curie temperature, (3) large energy band gaps, (4) large magnetic moment, and (5) being structurally compatible with other semiconductor materials typically employed in electronic devices (e.g., silicon and GaAs with respective lattice parameters of 5.4 and 5.6 Å).

Except NaVTe and CsNbZ with $Z = \text{Si, Ge, and Sn}$, all the compounds reported in Table I fulfill conditions (2), (3), and (4) above. Besides, compounds LiVSi (SC), LiVGe (SC), and NaVSi (HM) also fulfill (1) and (5), which indicates that these materials are in fact very promising for spintronics applications[16, 17]. Meanwhile, RbVTe (HM), CsVS (HM), and CsVSe (HM) fulfill (1)–(4) and only partially (5); however, the energy band gaps estimated for these compounds are so large that they also deserve to be highlighted. Finally, we mention RbNbTe as the most encouraging case of a HH HM not containing vanadium in the Y position; this alloy fulfills conditions (2)–(4), as many other compounds, but the corresponding $E_{\text{BG}}$, $E_{\text{HM}}$, and $T_c$ values are exceedingly large.

Overall, the most promising HH alloys for use in spintronics applications predicted by our computational re-

IV. CONCLUSIONS

We have performed a comprehensive first-principles study of the structural, electronic, structural, vibrational, and mixing properties of 90 $XYZ$ half-Heusler alloys ($X = \text{Li, Na, K, Rb, Cs; Y = V, Nb, Ta; Z = Si, Ge, Sn, S, Se, Te}$). In contrast to previous computational studies dealing with a large number of candidate materials, we have analyzed the magnetic features of most HH alloys at finite temperatures since this piece of information is crucial for guiding the experimental searches of technologically relevant materials. A total of 17 alloys are predicted to be vibrationally stable, half-metallic, and magnetically ordered at room temperature, with total magnetic moments of 2 and 4 $\mu_B$ and semiconductor band gaps in the range of 1–4 eV. On the other hand, all the HH alloys that have been identified as anti-ferromagnetic, 21 in total, turn out to be metallic. We have also found 2 new magnetic semiconductors that exhibit high thermodynamic stability and Curie temperatures. After analyzing the mixing stability of the vibrationally well-behaved HH alloys, we have identified the following compounds as overall most promising for spintronics applications: LiVSi (SC), LiVGe (SC), NaVSi (HM), RbVTe (HM), CsVS (HM), CsVSe (HM) and RbNbTe (HM). On the other hand, we have argued that simple doping strategies may be used to improve the mixing stability of some of the discarded HH half-metals. Hence, we hope that our computational study will stimulate new experimental efforts leading to progress in the field of spin-based electronics.

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