A new spin gapless semiconductors family: Quaternary Heusler compounds

G. Z. Xu¹, E. K. Liu¹, Y. Du¹, G. J. Li¹, G. D. Liu², W. H. Wang¹(a) and G. H. Wu¹

1 Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences Beijing 100190, PRC
2 School of Material Science and Engineering, Hebei University of Technology - Tianjin 300130, PRC

received 20 January 2013; accepted in final form 13 March 2013
published online 15 April 2013

PACS 71.20.-b – Electron density of states and band structure of crystalline solids
PACS 71.20.Lp – Intermetallic compounds
PACS 75.50.Cc – Other ferromagnetic metals and alloys

Abstract – By using first-principles calculations, we investigate the band structures of a series of quaternary LiMgPdSn-type Heusler compounds. Our calculation results show that five compounds, CoFeMnSi, CoFeCrAl, CoMnCrSi, CoFeVSi and FeMnCrSb, possess unique electronic structures characterized by a half-metallic gap in one spin direction while they have a zero-width gap in the other spin direction showing a spin gapless semiconducting behavior. We further analyse the electronic and magnetic properties of all quaternary Heusler alloys involved, and reveal a semi-empirical general rule (the total valence electrons number should be 26 or 28) for indentifying spin gapless semiconductors in Heusler compounds. The influences of lattice distortion and main-group element change have also been discussed.

Spin gapless semiconductors (SGS), as a new concept in spintronics, were first proposed theoretically and verified experimentally in doped Pd-based oxide materials by Wang in 2008 [1,2]. They can be regarded as a combination of gapless semiconductors [3] and half-metallic (HM) ferromagnets [4]. In gapless semiconductors, such as the first studied HgCdTe and HgCdSe, etc. [3], or the recently widely studied graphene [5], no threshold energy is required to excite the carriers from valence states to conduction states owing to the zero-width gap, thus achieving considerably higher electron mobility and more sensitive response to the external fields than the ordinary semiconductors. HM ferromagnets, in which conducting electrons are 100% spin polarized, are also attractive novel spintronic materials with an insulating or semiconducting gap in one spin direction, while in the other the electrons show a metallic behavior. In the case of SGS, for which the density-of-states (DOS) scheme is shown in fig. 1(a), the spin-down gap across the Fermi level is retained as in HM ferromagnets, but a zero-width gap appears in the spin-up direction, where the electrons show a gapless semiconducting behavior. The special DOS feature of SGS indicates some novel transport properties and applications in spintronic devices, considering that the conducting electrons or holes are not only 100% spin polarized but also easily excited. The design of SGS can be pursued either by introducing magnetism in gapless semiconductors [1,6,7] or by opening a zero bandgap in one spin channel based on the ferromagnetic semiconductors [8] or HM ferromagnets [9,10].

(a)E-mail: wenhong.wang@iphy.ac.cn
Recently, the Heusler alloy Mn$_2$CoAl, which was previously calculated to be a HM ferromagnet [11], was experimentally demonstrated to be a SGS material [9]. Later on, Galanakis et al. [10] calculated a series of inverse Heusler compounds and found several of them to be candidates for SGS. Heusler compounds [12] are a huge family with more than 1000 members, that have been applied in many areas owing to their multifunctionality and numerous properties [13]. They have innate advantages in spintronic devices due to the good compatibility with conventional semiconductors. In the present paper, we propose a new material family that possesses the properties of SGS: quaternary Heusler compounds.

Quaternary Heusler can be identified by $XX'YZ$ with 1:1:1:1 stoichiometry, where $X$, $X'$, $Y$ are transition metals and $Z$ are main-group elements. $XX'YZ$ crystallizes in a LiMgPdSn, otherwise called $Y$-type, structure [14] (as shown in fig. 1(b)) with space group $F43m$, where the $X$ and $X'$ atoms with more valence electrons occupy the 4a (A) and 4b (C) sites, respectively, the $Y$-atoms with less valence electrons occupy the 4c (B) sites, the main-group element $Z$ lies on the 4d (D) sites. The reliability of this occupation rule in quaternary Heusler alloys has been proved by both theoretical and experimental studies [15,16]. Those studies also imply that the $XX'YZ$ alloy tends to form a highly ordered structure rather than a disordered configuration. Based on the above structure, we have carried out systematic first-principles calculations by changing $X$, $X'$ from V to Co and $Y$ from Ti to Mn along the Periodic Table, while choosing Al or Si for $Z$. Our calculations used the CASTEP package [17,18] based on the pseudopotential method with a plane-wave basis set within the density functional theory (DFT). It should be pointed out that, however, the DFT calculations usually underestimated the fundamental bandgaps of semiconductors and insulators. However, some theoretical and experimental studies indicate that the half-metal bandgap of the Heusler compounds is likely not subject to this underestimation [19,20]. The exchange correlation energy was treated under the generalized gradient approximation (GGA) [21]. For all cases a plane-wave basis set cut-off energy of 400 eV and a mesh of $10 \times 10 \times 10$ $k$-points were employed to ensure good convergence. By performing the geometry optimization calculation, we obtained the equilibrium lattice constants.

As a result, our calculations have indentified four compounds that would be probable SGS: CoFeMnSi, CoFeCrAl, CoMnCrSi, CoFeVSi. Their nearly integral magnetic moments prove the existence of the HM gap, which is a prerequisite for being SGS. In addition, these alloys can be synthesized easily as they can be regarded as a combination of the full Heusler alloys $X_2YZ$ and $X'_2YZ$. For example, CoFeMnSi can be seen as the combination of Co$_2$MnSi and Fe$_2$MnSi, which has been successfully synthesized by Dai et al. [22]. In fig. 2 and fig. 3 the DOS of all these four alloys exhibit a bandgap in one spin channel and a typical energy valley approaching zero at the Fermi energy in the other spin channel, which fulfills the requirements of SGS as above described. The spin-resolved band structure of CoFeCrAl is given in fig. 2 as an example. An energy gap is opened in the minority-spin state across the Fermi energy as in a HM ferromagnet, the most eye-catching point is that in the majority-spin state the energy band touches the

![Fig. 2: (Color online) Part of the band structure and density of states (DOS) of CoFeCrAl: (a) majority spin, the green lines are used to emphasize, (b) density of states, (c) minority spin. The irreducible representations of $d$-orbital hybridized bands are given for the $\Gamma$-point, and are in accordance with those provided in fig. 5.](17007-p2)
A new spin gapless semiconductors family: Quaternary Heusler compounds

Fig. 3: (Color online) The spin-resolved density of states of CoFeMnSi, CoMnCrSi, CoFeVSi and FeMnCrSb. The positive DOS indicated by the blue filled area corresponds to the majority-spin state, the downward part indicated by the red color corresponds to the minority-spin state. The line located on the energy axis at zero is the Fermi level. It can be seen that the DOS of the four compounds all reveal a gap around the Fermi energy in the minority-spin direction and a valley approaching zero at the Fermi level in the majority-spin direction.

Fig. 4: (Color online) (a) A presentation of all the quaternary Heusler compounds that are calculated in this work, with theoretical equilibrium lattice parameters as one axis and total valence electrons $N_v$ as the other. The different background stands for the systems obeying the Slater-Pauling rule $M = N_v - 18$ (light yellow) and $M = N_v - 24$ (light blue), respectively. The compounds with 21 electrons lying in the boundary are usually nonmagnetic, i.e. they belong to neither region. The hollow squares represent the systems that deviate from the rule with noninteger magnetic moments. The red stars mark the composites that are suggested to be SGS, and Mn$_2$CoAl is shown for comparison. (b) Formation energy of the calculated quaternary Heusler compounds as a function of the lattice constant.
Fig. 5: (Color online) The sketch of possible hybridizations between the d-orbitals of transition atoms at different sites in the $XX'YZ$ quaternary Heusler compound (left for spin-down electrons, right for spin-up electrons). The symmetry representations of degenerated orbitals refer to the work by Galanakis et al. [22]. The green line indicates the location of the Fermi level, which is actually in the same position with respect to both spin directions.

Fermi level at $K$, $L$ (valence band) and $X$ (conduction band) points in the Brillouin zone, which corresponds to a valley in the DOS at the Fermi energy. This closed bandgap character in the majority-spin state suggests that CoFeCrAl is a SGS rather than a normal HM ferromagnet, and this deserves further experimental studies to be confirmed.

In order to illustrate in more detail the properties of quaternary Heusler compounds and search the possible rule for finding SGS that are underneath the superficial results, in fig. 4(a), we listed the calculated results in a two-dimensional graph taking the calculated equilibrium lattice parameters as one variable and the total valence electrons as the other. In order to investigate the structure stability of the above-constructed quaternary Heusler compounds, we also carried out the formation energy calculation. According to the definition: $E_{\text{form}} = E_{\text{total}} - E_X - E_{X'} - E_Y - E_Z$, where $E_{\text{form}}$ stands for the formation energy, $E_{\text{total}}$ represents the quaternary-compound energy, and $E_X$, $E_{X'}$, $E_Y$, and $E_Z$ represent the energy when each element crystallizes in pure metals. A negative $E_{\text{form}}$ value means that the compound can be stably synthesized. The calculated results shown in fig. 4(b) demonstrate that most compounds are stable except for two of them. We know that if there exists a bandgap in one spin direction, the magnetic moment of the compound is supposed to be integer and obey the Slater-Pauling rule [23,24]. In our cases, the magnetic moments of most of the composites involved follow the generalized Slater-Pauling rule $M = N_v - 24$ or $M = N_v - 18$ [25], indicated by the different background in fig. 4. There are some of the compounds containing V or Ti as Y-atom (marked by hollow squares) that deviate from the Slater-Pauling rule with smaller magnetic moments comparing with the estimated integer value. Out of the total number of valence electrons equal to 21, there are 12 or 9 spin-down electrons that occupy a level below the Fermi energy, while at the borderline of 21 electrons, some compounds become nonmagnetic, disobeying Slater-Pauling rule, which can be understood from consideration of the usual incompatibility of semiconducting and magnetism in one single-phase alloy, as in the case of 24 and 18 valence electrons. Remarkably, we noticed that the four compounds that were supposed to be SGS all have 26 or 28 valence electrons and the previous Mn$_2$CoAl was also a 26-electron system [9]. In order to justify that it is not coincidental but rather an effective criterion for being SGS, in what follows we carried out detailed discussions from the perspective of atomic hybridization.

Previously, there have been elaborated analyses of atomic hybridization and about the origin of the HM bandgap in the studies of Heusler-based HM
A new spin gapless semiconductors family: Quaternary Heusler compounds

Fig. 6: (Color online) Band structures of CoMnCrSi and CoFeCrGa/In, the blue (red) line represents the spin-up (down) electron. (a) The upper panel is the band structure of CoMnCrSi with equilibrium lattice constants, the lower one is with a uniaxial expansion of 4% while keeping the volume unchanged (the k path is different from the cubic one due to the reduced symmetry). (b) Partial band structures of CoFeCrGa and CoFeCrIn under equilibrium lattice constants.

ferromagnets [26]. Here for the sake of searching for SGS, one should take into account orbital hybridizations of both the spin-up and spin-down directions. For comparison, in fig. 5, we still present the schematic diagram of spin-down hybridization. In the system obeying the Slater-Pauling rule \( M = N_v - 24 \), the Fermi level is supposed to locate between the \( 3t_{1u} \) and \( 2e_u \) degenerate levels as shown in the figure. The gap between \( 3t_{1u} \) and \( 2e_u \), i.e., the energy gap of spin-down electrons around the Fermi level, is basically determined by the \( d \)-orbital hybridizations between the X-atom at the A site and the \( X' \)-atom at the C site. In the spin-up direction, the total number of energy levels and symmetry representations are identical to those in the spin-down direction, however, the relative position of the hybridization energy scale is moved by the exchange splitting in atoms both inside and in between.

Combining the results of all the band structures that we have obtained, the hybridization picture is proved to be similar except that in some systems \( 2e_u \) and \( 3t_{1u} \) may intersect at the \( \Gamma \)-point (not shown in the figure). According to the above-described hybridization scheme, we index the \( d \)-orbital hybridized bands of CoFeCrAl in fig. 2 using the corresponding representations. Now let us re-examine the condition for being SGS, which also needs a gap existing around the Fermi level as in the spin-down state, only that the bandgap width is zero. We conclude that the way to guarantee that the Fermi level falls in between a bandgap is that it should not locate in those degenerate bands; otherwise it must cut the band without a gap. In other words, it is required that the total valence electrons be 26 or 28, with the Fermi level located between \( 2e_u \) and \( 2e_g \) (shown in fig. 5) or \( 2e_g \) and \( 3t_{2g} \) orbitals. We can take the band structure of CoFeCrAl (fig. 2) as an example to interpret this. There, the Fermi level was located between the \( 2e_g \) and \( 2e_u \) orbitals, and in the meantime, the top of the \( 2e_u \) bands and the bottom of the \( 2e_g \) bands exactly touch each other at the Fermi level, thus showing SGS properties. If the total valence electrons were subtracted by unity or added by unity, the Fermi level would move down or up. Because the \( 2e_u \) or \( 2e_g \) are degenerated in some \( k \)-points, the Fermi level must cut the entangled bands in order to contain one electron more or one electron less. In this sense, the compounds with 25 or 27 valence electrons cannot be the candidates of SGS. How about locating the Fermi energy between the lower degenerate orbitals, i.e., \( 2e_u \) and \( 3t_{1u} \) or \( 3t_{1u} \) and \( 3t_{2g} \)? They can be excluded from our consideration because they correspond to the total of 24 and 21 valence electrons, which are usually nonmagnetic according to the above discussion. Finally we can draw the conclusion that the prerequisite for finding SGS in this quaternary Heusler system is to make the total valence electron number equal to 26 or 28. Based on this rule, we have calculated another compound with 26 valence electrons: FeMnCrSb, and as we expected, its DOS structure (shown in fig. 3) reveals the character of SGS.

Moreover, the above rule is not only reasonable in the quaternary Heusler alloys that we considered in this work, it can be also applied to other Heusler compounds as long as the unit cell contains four atoms; Mn_2CoAl is such a...
case. Nevertheless, it should be noted that the valence electron number is a necessary but not sufficient condition to identify SGS. The total valence electron number can only decide the electrons that occupy a level below the Fermi energy, but the detailed band structure around the Fermi level which changes with different compositions is not indicated. For instance, Fe$_2$MnAl has 26 valence electrons but it is not a half metal [27], therefore the fundamental condition is not fulfilled; Co$_2$MnAl [28] is a well-known HM ferromagnet with 28 electrons, but in the spin-up direction, the upper and lower band are both cut by the Fermi level. Finally, we should point out here that the unique band structure of quaternary Heusler SGS can be tuned by stretching or contracting or even tetragonally distorting the lattice. The band structures of CoMnCrSi with equilibrium lattice parameters and uniaxial distorted lattice are exhibited in the upper and lower panel of fig. 6(a), respectively. Ignoring the Brillouin zone change caused by the broken cubic symmetry, it can be clearly seen that the spin-up band exactly touches the Fermi level after distortion, though the spin-down gap becomes a little smaller as well. On the other hand, the substitution of $sp$-elements by atoms in the same group can also destroy the electronic structure of SGS. For instance, as shown in fig. 6(b), when we use isoelectronic Ga or In to replace Al in CoFeCrAl, the spin-up band mainly keeps unchanged while the spin-down gap is destroyed due to the overlapping of 3$Z_{1u}$ and 2$e_u$, which can be attributed to the weakening of the covalent hybridization between the main-group and transition atoms.

In conclusion, we have performed first-principles calculations on a series of quaternary Heusler compounds and finally found five compounds, CoFeMnSi, CoFeCrAl, CoMnCrSi, CoFeVSi and FeMnCrSb, that are identified as potential candidates for SGS from the DOS and band structure characteristics. The former four compounds ought to be easily synthesized and high Curie temperatures are expected when regarding them as a combination of $X_2YZ$ and $X_2YZ$, making them promising spintronic devices. In addition, a general rule for which the valence electron number is 26 or 28 is summarized in the search for SGS among Heusler compounds. This semi-empirical rule can narrow the scope of finding SGS in the future. Nevertheless, as it is a necessary but not sufficient condition, specific systems should be treated differently and the alteration of $sp$ atoms in the same group may cause a considerable change of the electronic properties.

***

This work was supported by National Natural Science Foundation of China (Grant Nos. 51171207 and 51071172) and National Basic Research Program of China (973 Programs: 2012CB619405).

REFERENCES