MATERIALS SCIENCE

First-principles design of spintronics materials

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ABSTRACT

Spintronics is one of the most promising next generation information technology, which uses the spins of electrons as information carriers and possesses potential advantages of speeding up data processing, high circuit integration density, and low energy consumption. However, spintronics faces a number of challenges, including spin generation and injection, long distance spin transport, and manipulation and detection of spin orientation. In solving these issues, new concepts and spintronics materials were proposed one after another, such as half metals, spin gapless semiconductors, and bipolar magnetic semiconductors. Topological insulators can also be viewed as a special class of spintronics materials, with their surface states used for pure spin generation and transportation. In designing these spintronics materials, first-principles calculations play a very important role. This article attempts to give a brief review of the basic principles and theoretical design of these materials. Meanwhile, we also give some attentions to the antiferromagnetic spintronics, which is mainly based on antiferromagnets and has aroused much interest in recent years.

Keywords: spintronics, antiferromagnetic spintronics, half metals, magnetic semiconductors, topological insulators

INTRODUCTION

Information technology is one of the important issues in the 21st century. As the Moore law gradually loses its effect, conventional charge-based electronics will come to the end in the near future. Developing alternative high speed and low energy consuming information technology is urgently needed. Up to now, many new methodologies have been proposed, such as molecular electronics, nanoelectronics, spintronics, and quantum information techniques, among which spintronics is one of the most promising ones. Compared to other methodologies, spintronics is compatible with conventional electronics, thus many techniques used in conventional electronics can be directly extended to spintronics.

Different from conventional electronics, which uses the electron’s charge degree of freedom for information processing, spintronics is devoted to incorporating the electron’s spin degree of freedom. In an ideal situation, there will be purely spin current and no charge current in the spintronic circuit, thus no heat will be created and wasted. Meanwhile, information will be transmitted at a high speed owing to the spin coherence effect [1].

The discovery of giant magnetoresistance (GMR) [2,3] is regarded as the beginning of spintronics. In a spin valve device constructed by two layers of ferromagnetic metals sandwiching one layer of non-magnetic metal, the conductivity across the device differs by an order of magnitude when the magnetization directions in the two ferromagnetic metals are made parallel or antiparallel to each other by applying an external magnetic field. The conductivity difference can be even larger when replacing the middle layer by a non-magnetic insulator. Such a GMR effect can be exploited to make two-state memory cells and switches. The well-known applications of GMR now are magnetic field sensors used to read data in hard disk drives, and magnetoresistive random-access memory.

Despite its great potential advantages, spintronics now faces a number of challenges, such as generation of fully spin-polarized carriers (pure spins) and injection of spin into devices, long distance spin transport, and manipulation and detection of carriers’ spin orientation. The solutions to these issues rely on the development of device fabrication and optimization techniques on one hand, and designing
new spintronics materials with specific properties on the other hand. Pure spin generation and injection mainly depends on the degree of spin polarization in the used semiconductors or metals. Meanwhile, the spin scattering at the metal–metal or metal–semiconductor interface is also important. Although many efforts have been made, to obtain 100% spin polarized carriers at room temperature remains a challenging job. Thanks to the discovery of carbon-based nanomaterials such as graphene and carbon nanotubes [4], the challenge of long distance spin transport is likely to be solved in the near future. Because of their very weak spin–orbit coupling (SOC), carbon-based nanomaterials can have a long spin coherence length up to a few micrometers, thus are ideal spin transportation materials. As with spin manipulation and detection, there are some methods based on the coupling effects between spin and light, magnetic field, electric field, etc. For example, by applying an external magnetic field, one can switch the carrier’s spin orientation by reversing the material’s spontaneous magnetization, which is however hard to control in both time and spatial scales, especially when the device size is reduced to nanoscale. This is because magnetic field is hard to be applied locally, i.e. it may produce undesirable effect on neighboring device parts. Moreover, the reversion of macroscopic spontaneous magnetization is relatively slow due to the phenomenon of magnetic hysteresis.

To solve the above issues, diverse spintronics materials have been designed. According to their electronic and magnetic properties, spintronics materials can be classified as magnetic metals, topological insulators (TIs), and magnetic semiconductors (Fig. 1a). In a spintronic circuit, magnetic metals and TIs serve as spin sources and drains, while magnetic semiconductors constitute the central region of the device. In the three components, spin manipulation/detection can be performed separately based on the coupling effects between spin and light, magnetic field or electric field (Fig. 1b).

In general, practical spintronics materials should have a robust magnetic order at room temperature, i.e. their magnetic ordering temperature should be notably higher than room temperature. Meanwhile, large spin polarization around the Fermi energy level is preferred. In the following, we review the basic properties and applications of existing spintronics materials.

**Magnetic metals and TIs**

**Ferromagnetic metals**

Ferromagnetic metals include Fe, Co, Ni metals, and also their alloys. They are the oldest spintronics materials that were used to construct spin valves and magnetic tunnel junctions. These materials are abundant and cheap, and can be handled easily. However, they can only supply partially spin-polarized carriers due to their low degree of spin polarization (Fig. 2a).

**Half-metallic ferromagnets**

Half-metallic ferromagnets (HMFs) were proposed by de Groot and Mueller [5]. Their fundamental characteristic lies in the electronic structure (Fig. 2b): one spin channel possesses metallic conduction while the other spin channel is...
insulating or semiconducting. Thus, HMFs can intrinsically provide single spin channel electrons, with the spin polarization reaching 100%. HMFs can be used for pure spin generation and injection. To develop practicable spintronic devices with HMFs, besides a high ferromagnetic Curie temperature, the half-metallic gap should also be wide enough to efficiently prevent the thermally agitated spin-flip transition and preserve half-metallicity at room temperature. Moreover, for magnetoelectronics applications, large magnetic anisotropy energy is favored [6]. Typical HMFs are CrO$_2$ [7,8] and Fe$_3$O$_4$ [9,10].

**Figure 2.** Schematic plots of band structures for various spintronics materials: (a) ferromagnetic metals, (b) half metals, (c) TIs, (d) HSCs, (e) SGSs, and (f) BMSs.

**Half-metallic antiferromagnets**
As a special type of half metals, half-metallic antiferromagnets (HMAFMs) can also provide 100% spin-polarized electrons, while showing no macroscopic magnetization [11,12]. The basic idea of HMAFMs is that for a half metal with stoichiometric composition, the spin magnetization per unit cell should be an integer in units of Bohr magneton and this integer can be zero after careful design. Because of zero net magnetization, half-metallicity of HMAFMs will keep unchanged under an external magnetic field. Also HMAFMs will not interfere with others magnetically. Thus, HMAFMs are very useful in some special situations, such as making the tip of spin-polarized scanning tunneling microscope. It should be noted that HMAFMs have not been verified in experiment yet.

**Topological insulators**
TIs are a special type of insulators, which are insulating in their bulk but metallic on their surface (Fig. 2c). Moreover, the metallic surface states are symmetry protected. Interestingly, the spin-up and spin-down electrons propagate in opposite direction on the surface [13]. Thus, TIs are ideal for pure spin generation and transport, without bringing any net charge current. Typical examples of TIs are HgTe [14] and Bi$_{1-x}$Sb$_x$ [15]. All TIs realized so far can only work at low temperatures, and still have a long way to go before their practical applications.

**Magnetic semiconductors**
Magnetic semiconductors, combing the properties and advantages of both magnets and semiconductors, form the basis for spintronics. Magnetic semiconductors can be applied for spin generation and injection, and spin manipulation and detection. Compared to other spintronics materials, magnetic semiconductors can be easily implemented in devices by utilizing nowadays well-developed semiconductor technology. Unfortunately, most magnetic semiconductors suffer from low magnetic ordering temperatures, hindering their practical applications.

In general, magnetic semiconductors can be divided into two categories: diluted magnetic semiconductors (DMSs) and intrinsic magnetic semiconductors. Furthermore, based on different electronic and magnetic properties, intrinsic magnetic semiconductors can be subdivided into half semiconductors (HSCs), spin gapless semiconductors (SGSs), bipolar magnetic semiconductors (BMSs), and asymmetric antiferromagnetic semiconductors (AAFMSs).

**Diluted magnetic semiconductors**
DMSs are obtained from traditional non-magnetic semiconductors by doping with small amount of magnetic ions [16–20]. The two key elements of DMSs are carrier doping and magnetic doping, which can be realized simultaneously by doping with the same ions or respectively with successive two-step doping. The doped carriers mediate ferromagnetic exchange interactions between diluted magnetic ions, with the magnetic order probably up to room temperature [21]. Typical DMSs include the well-known (Ga,Mn)As, where Mn introduces both carriers and magnetism [16], Li$_{1+x}$(Zn,Mn)As in which the excess Li introduces carriers while Mn introduces local spins [18], and so on. The advantage of DMS is that it can be easily fabricated, but it faces the problems of not high spin polarization, low dopant solubility, secondary phase separation, and
bad controllability. See recent reviews about DMSs [22–24].

**Half semiconductors**

HSCs are semiconductors in one spin channel but insulators in the other spin channel. Their valence band (VB) and conduction band (CB) are spin split with the valence band maximum (VBM) and conduction band minimum (CBM) possessing the same spin channel (Fig. 2d). Since VBM and CBM are fully spin polarized, HSC can generate 100% spin-polarized electrons and holes under thermal or optical excitation or simply by electrical gating. HSC can be characterized by three energy gaps, the spin-flip gap $\Delta_1$ in VB, band gap $\Delta_2$, and spin-flip gap $\Delta_3$ in CB. For practical applications, big spin-flip gaps and small band gap are preferred. Typical examples of HSCs include La$_2$NiMnO$_4$ [25], BiMnO$_3$ [26], and V(TCNE)$_x$ [27].

**Spin gapless semiconductors**

SGSs were proposed by Wang [28]. They are a subclass of gapless semiconductors, in which VBM and CBM touch with each other exactly at the Fermi energy level. For SGS, at least one of the VBM and CBM is fully spin polarized (Fig. 2e). The combination of spin polarization and zero gap endows SGS diverse interesting properties and potential applications. For example, no threshold energy is needed to excite an electron from VB to CB and the excited carriers can be fully spin polarized. Meanwhile, due to quadratic or linear energy band dispersion, carrier mobility of SGS is about two to four orders of magnitude higher than that of traditional semiconductors. What is more, the electronic structure of SGS is very sensitive to external effects such as pressure and magnetic field, thus can be tuned for various applications in spintronics, optics and sensors [29]. The concept of SGS has been verified experimentally in Heusler compound Mn$_2$CoAl [30], but its family members are still much limited.

**Bipolar magnetic semiconductors**

BMSs [31] are characterized by a unique electronic structure, where VBM and CBM are fully spin polarized in the opposite spin direction (Fig. 2f). Similar to HSCs, BMS can also be described by three energy gaps, the spin-flip gap $\Delta_1$ in VB, band gap $\Delta_2$ and spin-flip gap $\Delta_3$ in CB. The difference between HSC and BMS lies in their spin polarization direction at VBM and CBM.

The proposal of BMS is aimed to realize electrical control of carriers’ spin orientation, since electric field can be easily applied locally, in contrast to magnetic field. In BMS, completely spin-polarized currents with reversible spin polarization can be created and controlled simply by applying a gate voltage (Fig. 3). Under zero gate voltage ($V_G = 0$), BMS exhibits intrinsic semiconducting behavior. Under an appropriate negative gate voltage ($V_G < 0$), when the Fermi level is shifted down into the spin-flip gap $\Delta_1$, BMS possesses half-metallic conduction with the carriers fully spin polarized in the spin-up direction. While the Fermi level shifts up into the spin-flip gap $\Delta_3$ under an appropriate positive gate voltage ($V_G > 0$), BMS also possesses half-metallic conduction but with the carriers fully spin polarized in the spin-down direction. Through this way, the carrier’s spin orientation in BMS can be easily reversed just by altering the sign of the applied gate voltage. Based on BMS, several electrically controlled spintronics devices have been developed, such as bipolar field effect spin filter and field effect spin valve. BMS can also be used to detect and separate entangled electrons from superconductors, which is very attractive in quantum information processing [32].

The existence of BMS materials has been verified by theoretical prediction and subsequent successful fabrication of MnPSe$_3$ nanosheets [33,34]. However, the electrical control of spin orientation in such materials has not been measured yet. This needs further experimental studies.

**Asymmetric antiferromagnetic semiconductors**

AAFMSs were proposed very recently [35]. They serve as a general scheme to obtain magnetic semiconductors with both room-temperature magnetic ordering and large spin polarization. In AAFMSs, magnetic moments are designed to be carried by different transition-metal ions and cancelled out by each other through antiferromagnetic coupling. The strong antiferromagnetic superexchange interaction results in a high magnetic ordering temperature. Meanwhile, the magnetic orbital energy mismatch among different transition metals induces highly spin-polarized VB and CB states. Li et al. suggest the
Figure 4. The possible d orbital energy mismatches between two magnetic ions M1 and M2 in an octahedral crystal field. M1 and M2 ions are assumed to have a $t_{2g}^{3}e_{g}^{0}$ electron configuration and be antiferromagnetically coupled. Adapted from Ref. [35] with permission. Copyright 2015 American Physical Society.

double perovskites $A_{2}CrMO_{6}$ ($A =$ Ca, Sr, Ba; $M =$ Ru, Os) as potential AAFMSs, which however need further experimental verification.

The power of AAFMS is that by tuning the interplay of crystal field splitting, spin exchange splitting, and magnetic orbital energy position, various types of room-temperature magnetic semiconductors such as HSC, SGS, and BMS can be obtained. For example, considering two magnetic ions in an octahedral crystal field with $t_{2g}^{3}e_{g}^{0}$ electron configuration, where the first ion has a small spin exchange splitting $\Delta_{s}$ than crystal field splitting $\Delta_{t}$, while the second one has a big spin exchange splitting compared to crystal field splitting (Fig. 4). Supposing the two magnetic ions are antiferromagnetically coupled, which is consistent with Goodenough–Kanamori rules, one can achieve an SGS when the empty spin-down $t_{2g}$ orbital of first ion touches with the occupied spin-down $t_{2g}$ orbital of second ion (Fig. 4a). Gradually increasing the first ion’s d orbital energy relatively, the material evolves from SGS to HSC and again to SGS (Figs 4b–d). All the materials are expected to have a high magnetic ordering temperature owing to the strong antiferromagnetic superexchange interaction.

**THEORETICAL DESIGN OF SPINTRONICS MATERIALS**

Spintronics materials are the basis of spintronics. Although lots of spintronics materials have been proposed previously, most of them are far from practical applications due to a number of problems, such as the destruction of half-metallicity by spin-flip transitions, low magnetic ordering temperature, difficulty in synthesis, and bad controllability. To design spintronics materials that work at room temperature and that can be easily manipulated in experiment is the key to bring spintronics to real life.

In this aspect, first-principles calculations provide us with a powerful and cheap tool. Compared to experimental materials design, which is a trial and error job, consuming much time and energy and inevitably causing a waste of experimental resources, first-principles calculations do not need any real sample and can be performed even for materials that have not been synthesized yet. By first-principles calculations, the properties of materials can be routinely predicted, based on which one selects those with required properties, and confirms them by a followed experiment. Such a procedure can largely reduce the period of materials design. Moreover, thanks to the development of computer technology and theoretical chemistry, the speed and accuracy of first-principles calculations have both been significantly improved.

In the following, the progresses in first-principles design of spintronics materials including half metals, TIs, and magnetic semiconductors are reviewed.

**Half metallic ferromagnets**

Transition-metal oxides

Transition-metal oxides such as CrO$_2$ and Fe$_3$O$_4$ are the oldest HMFs. Although they were widely used for their magnetic properties, the half-metallicity in these oxides remained unknown until it was revealed by first-principles calculations [7,9]. Now, the half-metallicity of CrO$_2$ and Fe$_3$O$_4$ has been well established by point contact Andreev reflection and spin-resolved photoelectron spectroscopy [8,10].

Transition-metal chalcogenides and pnictides

In order to explore HMFs that are compatible with the III-V and II-VI semiconductors, many efforts have been done in designing HMFs with the zincblende and wurtzite phases of transition-metal chalcogenides and pnictides.

Zincblende phase of CrAs was first proposed to possess half-metallic conduction based on first-principles calculations [36], and was fabricated in thin film form by molecular-beam epitaxy, which
showed a ferromagnetic behavior at room temperature \([36–38]\). Followed by CrAs, CrSb, and MnAs, thin films or nanodots were also successfully grown \([39,40]\), which were predicted to be (quasi-) half metals \([41,42]\).

Because zincblende phases of CrAs, CrSb, and MnAs are very high in energy compared to the nickel–arsenide ground phase and also very soft against crystalline deformations, the growth of high-quality samples seems very difficult \([43]\). Thus, researchers gradually turned their attentions to other possible compounds.

Based on first-principles calculations, Mavropoulos and Galanakis performed systematic search for HMFs in zincblende phase of \(XY\), with \(X = \text{V}, \text{Cr}, \text{and Mn}\) and \(Y = \text{N, P, As, Sb, S, Se, and Te}\) \([44]\). After considering the lattice mismatch with commonly used semiconductors and the evolution of half-metallicity with strained lattice constants, the authors found that VAs, VSb, CrAs, CrSb, VTe, CrSe, and CrTe are the best candidates for HMFs. They also studied the transition-metal terminated (001) surfaces, and found that the half-metallicity is maintained in most cases.

The theoretical studies of Liu \textit{et al.} also suggest the zincblende phase of CrTe, CrSe, and VTe to be excellent HMFs with large half-metallic gaps (up to 0.88 eV) \([45]\). The authors found that the three compounds are approximately 0.31–0.53 eV per formula higher in energy than the corresponding nickel–arsenide ground phase. These values are significantly smaller than those for the already fabricated CrAs, CrSb, and MnAs (around 1 eV). Meanwhile, their bulk moduli and shear moduli are higher or comparable to those of CrAs. Thus, these compounds may be more easily grown epitaxially in the form of thin films.

Liu \textit{et al.} also studied systematically all the 3d transition-metal pnictides and chalcogenides in the wurtzite phase, and identified nine potential HMFs, i.e. MnSb, CrAs, CrSb, VAs, VSb, CrSe, CrTe, VSe, and VTe \([46]\). These HMFs have large half-metallic gaps (up to 0.97 eV), and quite low energies (down to 0.31 eV) per formula with respect to the corresponding ground-state phases. Their bulk moduli are approximately equivalent to those of typical binary III-V and II-VI semiconductors, such as GaAs and InAs.

Though the theoretical works done, the experimental verification is still scarce except for CrAs, CrSb, and MnAs.

**Double perovskites**

Double perovskites \(A_2M'M''O_6\) are based on the perovskite structure \(AMO_3\), with the transition-metal sites \(M\) being occupied alternately by different cations \(M'\) and \(M''\) (Fig. 5a). Double perovskites possess the advantages of very simple crystal structures, potentially a very large number of members, and strong coupling between magnetic ordering and electronic properties. In \(A_2M'M''O_6\), the transition metals \(M'\) and \(M''\) both can carry a magnetic moment, and in most cases are coupled ferrimagnetically or antiferromagnetically with each other.

Double perovskites played an important role in the development of the concept of half metals. The first breakthrough was made by Tokura \textit{et al.} in \(Sr_2\text{FeMoO}_6\), which exhibits an intrinsic tunneling-type magnetoresistance at room temperature \([47]\). First-principles calculations revealed that \(Sr_2\text{FeMoO}_6\) is an HMF (ferrimagnet), where the spins of \(S = S/2\) carried by the \(\text{Fe}^{3+}\) ions are ferrimagnetically coupled with the spins of \(S = 1/2\) carried by the \(\text{Mo}^{5+}\) ions, resulting in a total spin magnetic moment of 4 \(\mu_B\). Because of the strong hybridization among the \(\text{Mo} 4d, \text{Fe} 3d\) and \(\text{O} 2p\) states, the density of states for the spin-down channel crosses with the Fermi level, whereas the spin-up channel opens a gap.
at the Fermi level, leading to a half-metallic behavior [47].

Followed by Sr$_2$FeMoO$_6$, a similar compound Sr$_2$FeReO$_6$ was designed by the same group [48]. First-principles calculations predicted Sr$_2$FeReO$_6$ as a half metal with the spins of Fe$^{3+}$ and Re$^{5+}$ ions ferrimagnetically coupled with each other, which are consistent with the experimental measurements of electronic and magnetic properties [48].

Other double perovskites like La$_2$CrCoO$_6$, La$_2$VFeO$_6$ are also potential HMFs [49].

Heusler alloys

Heusler alloys consist of a large number of members, and have been intensively studied for their diverse magnetic phenomena, such as ferromagnetic ordering and high Curie temperature. Heusler alloys crystallize in a close-packed cubic structure, of which the unit cell is that of an fcc lattice with four atoms as basis at (0 0 0), (1/4 1/4 1/4), (1/2 1/2 1/2), and (3/4 3/4 3/4) in Wyckoff coordinates (Fig. 5b). According to the different elements residing at the four sites, Heusler alloys can be classified into ternary Heusler alloys and quaternary Heusler alloys. Ternary Heusler alloys can be subdivided into half Heusler alloys with the chemical formula X$_2$YZ, where X and Y are transition-metal atoms and Z is a main-group element, and full Heusler alloys with the chemical formula X$_3$YZ. In half Heusler alloys, the energetically most stable occupation sequence along the diagonal is X-Y-void-Z, while in full Heusler alloys, the sequence is X-Y-X-Z when the valence of X is larger than Y, or X-X-Y-Z when the valence of Y is the largest. The latter is also called as inverse Heusler alloys. For quaternary Heusler alloys, the chemical formula is identified by XX’ YZ, where the valence of X is larger than X’, and X’ is larger than Y. The preferred occupation sequence along the diagonal is X-Y-void-Z. Based on first-principles calculations, Galanakis et al. have systematically studied the electronic and magnetic properties of the Heusler alloy family, and found most of them obey the Slater–Pauling rule, which state that the total spin magnetic moment $M_s$ of the unit cell scales as a function of the total number of valence electrons $Z_v$, following the relation $M_s = Z_v - n$. The integer n is determined by the type of Heusler alloys [50–53]. These Heusler alloys following the Slater–Pauling rule are candidates for half metals and magnetic semiconductors.

NiMnSb is the first half Heusler alloy that was proposed to be an HMF by de Groot and Mueller [5], and now its half-metallicity has been well established in experiment [54]. Half Heusler alloys can be HMFs when they obey the rule of $M_s = Z_v - 18$, such as in the case of the NiYSb and CoYSb compounds, where Y accounts for V, Cr, and Mn [50]. Such a relation can be simply understood that a Heusler alloy having 18 valence electrons per unit cell is isoelectronic to inert gas and particularly stable, which tends to be a non-magnetic semiconductor, and for a Heusler alloy with $Z_v \neq 18$, the extra or missing electrons enter into only one spin channel.

For half-metallic full Heusler alloys, they obey the rule of $M_s = Z_v - 24$, which is different from half Heusler alloys and can be understood based on group theory analysis of d orbital hybridization of neighboring atoms. Examples of half-metallic full Heusler alloys are Co$_2$MnX ($X = Al, Ga, Si, Ge, Sn$) [51].

Inverse Heusler alloys follow three different variants of the Slater–Pauling rule, depending on the chemical type of the constituent transition-metal atoms. For $X = Sc$ and Ti, the alloys obey the relation of $M_s = Z_v - 18$; for $X = Cr$ and Mn, the relation reads $M_s = Z_v - 24$; Y is Cu and Zn results a relation of $M_s = Z_v - 28$. Note that V-based Heusler alloys can follow both the relations of $M_s = Z_v - 18$ and $M_s = Z_v - 24$. Half-metallic inverse Heusler alloys include Sc$_2$CrAl, Ti$_2$NiAl, Mn$_2$ZnSi, and so on [52].

In the quaternary Heusler alloy family, there also exist a number of HMFs, which show a Slater–Pauling rule of $M_s = Z_v - 18$ or $M_s = Z_v - 24$ [53].

As can be seen above, by altering the three or four different composite elements, Heusler alloys provide a fertile soil for exploring HMFs.

**Organic and organometallic nanostructures**

Organic and organometallic materials have the potential advantages of easy synthesis and processing, good optoelectronic response, and long spin coherence length. Therefore, they are the focus of electronics and spintronics. In particular, the discovery of single layer graphene [4] and its fascinating properties [55–57] stimulates a fever of 2D materials, including graphitic BN, SiC, transition-metal dichalcogenides, silicone, germanene, and stanine [58–64]. However, most of these materials are non-magnetic, and the introduction of ordered spin and even half-metallicity is a challenging job. Based on first-principles calculations, some schemes or structures have been proposed.

Considering the magnetism of transition metals, a natural way to realize spin ordering in non-magnetic organic systems is forming hybrid organic transition-metal composites. For example, by filling BN nanotubes with Ni hexagonal close-packed nanowires, Xiang et al. reported for the first time that a 100% spin polarization is achieved [65]. Also, they designed a class of 1D transition...
and magnetic moments of transition metals M

\( M \) tend to be a quasi-HMF, and (A

P, As, Sb) which have 18 valence electrons, in which the Heusler alloys can superexchange interact with the pairs (Fig. 6a). They found 2D MnPc sheet is an HMF with a Curie temperature of about 212 K [68].

It is also possible to realize half-metallicity without introducing transition metals. The first breakthrough was made by Louie et al. in graphene nanoribbons [69]. Graphene nanoribbons are known to possess two spin-polarized edge states, which are antiferromagnetically coupled to each other. Based on first-principles calculations, Louie et al. suggested applying an external transverse electric field to break the symmetry between the two edge states and induce half-metallicity. However, using more accurate calculation method, Kan et al. later proved that the required critical electric field is too high to achieve [70]. Alternatively, they provided a more realistic method, i.e. modifying each edge with a donor and an acceptor chemical group, respectively, which can introduce an effective transverse electric field due to the large dipole formed between the two groups (Fig. 5c). After careful selection, half-metallicity is realized in the ribbons with NO3 groups at one edge and CH3 groups at the other edge [71]. Later, based on experiment, Kan et al. constructed a free-standing 2D dimethylmethylene-bridged triphenylene (DTPA) porous sheet [72]. DTPA is characterized as a triangular graphene nanoflake with the central C atom substituted by an N atom (Fig. 6b). Such substitution induces a magnetic moment of 1 \( \mu_B \) in DTPA, which was predicted to be ferromagnetically ordered. The 2D DTPA sheet is an intrinsic HMF without external modifications. Near the same time, Du et al. predicted another experimentally synthesized graphitic carbon nitride (g-C3N4) to be a metal-free HMF [73]. This structure can be viewed as the well-known non-magnetic g-C3N4 sheet [74] with the linking N atom substituted by a C atom, which introduces a spin-polarized hole in the system (Fig. 6c).

Half-metallic antiferromagnets

Double perovskites

In double perovskites \( A_2M’M”O_6 \), the magnetic moments of transition metals \( M’ \) and \( M” \) tend to be coupled antiferromagnetically with each other due to the strong \( M’-O-M” \) superexchange interaction. By selecting appropriate \( M’-M” \) pairs with equal spins, an HMAFM with compensated magnetism can be obtained. For example, Pickett made a theoretical search in \( La_2M’M”O_6 \) with the pairs \( M’M” \) being MnCo, CrFe, CrRu, CrNi, MnV, and VCu, and found two HMAFMs at the fixed cubic structure, i.e. \( La_2VMnO_6 \) and \( La_2VCuO_6 \) [75]. Later, another two HMAFMs, \( K_2MnRhO_6 \) and \( La_2CrWO_6 \), were identified in an extended search by the same group [76]. Other potential HMAFMs are \( LaAVRu_6O_{16}, LaAVOsO_{16}, \) and \( LaAMoYO_6 \) (\( A = Ca, Sr, Ba; Y = Re, Tc) [77,78].

Heusler alloys

Most Heusler alloys obey the Slater–Pauling rule in the form of \( M_i = Z_i – n_i \), as stated above. A special case is \( Z_i = n_i \), in which the Heusler alloys can be non-magnetic semiconductors, or half metals and magnetic semiconductors with compensated magnetism. For example, \( Cr_2CoGa \) crystalizes in the inverse Heusler alloy structure and has a total valence electrons of 24. According to the Slater–Pauling rule of \( M_i = Z_i – 24 \), the total magnetic moment equals zero. First-principles calculations revealed that the material is a half metal with 100% spin polarization [79]. A similar case is \( Cr_2FeGe \). Following this idea, other HMAFMs can be found in half Heusler alloys \( CrMnZ (Z = P, As, Sb) \) which have 18 valence electrons, and full Heusler alloys \( Cr_2MnZ (Z = P, As, Sb, Bi) \) and \( Mn_2MnX (X = Al, Ga) \) which have 24 valence electrons [80–82].

Transition-metal chalcogenides and pnictides

FeAs and FeSe layers (Fig. 5d) are the key ingredient for Fe-based superconductors [83], in which Fe atoms are tetrahedrally coordinated by As or Se atoms and take a formal +2 state, bearing a high spin of \( S = 2 \). In the undoped case, they are antiferromagnets with striped or checkerboard magnetic

**Figure 6.** Three typical organic and organometallic nanostructures that were predicted to possess half-metallicity: (a) Mn-embedded phthalocyanine-based single porous sheet (Reproduced from Ref. [67] with permission. Copyright 2011 American Chemical Society.), (b) DTPA porous sheet (Reproduced from Ref. [72] with permission. Copyright 2012 American Chemical Society.), and (c) graphitic carbon nitride (g-C3N4) sheet (Reproduced from Ref. [73] with permission. Copyright 2012 American Physical Society.).
ordering. These structures can be utilized to design HMAFMs by alloying another transition metal Cr with Fe, where Cr$^{2+}$ ion also carries a high spin of $S = 2$. For example, substitution of Cr$^{2+}$ ions for half of the Fe$^{2+}$ ions in LaFeAsO, the antiferromagnetic nature of the system remains, and a HMAFM was gained \cite{84}. Similar results were found in BaFeAs$_2$, SrFeAsF, and $\alpha$-FeSe \cite{85,86}.

On the other hand, by assuming a chalcopyrite CuFeS$_2$ structure, Nakao found another type of HMAFMs: CrFeX$_2$ and VCoX$_2$ (X = S, Se, and Te) \cite{87}. As isoelectronic systems, MnCoN$_2$ and CrNiN$_2$ were also identified as potential HMAFMs not only in chalcopyrite structure, but also in NiAs-type, NaCl-type, zincblende, and wurzite structures \cite{88}. However, for other transition-metal pnictides with X = P, As, Sb, and Bi, because of strong hybridization between the transition metal and pnictide ions, HMAFM state could not be found.

Half-metallic diluted antiferromagnetic semiconductors

It is possible to obtain HMAFMs in non-magnetic semiconductors doped with equal amount of two different magnetic ions, which was proposed by Ogura and Akai \cite{89}. To obtain a compensated magnetic moment, the sum of $d$ electrons of the two transition-metal ions should be 10. For II-VI semiconductors, the appropriate transition-metal pairs are TiNi, VCo, and CrFe, while they are CrNi and MnCo for III-V semiconductors. Based on first-principles calculations, Ogura and Akai verified such a concept in (Zn$_{1-x}$Cr$_x$Fe)$_2$S and (Zn$_{1-x}$V$_x$Co)$_2$S \cite{89}. Later, they also explored the possibility of realizing half-metallic diluted antiferromagnetic semiconductors in other structures, such as chalcopyrite-type AgGaS$_2$ and CuAlS$_2$ \cite{90}. Another example is Os and Mo codoped TiO$_2$ \cite{91}.

Topological materials

Since there are already some reviews \cite{92–95} about traditional inorganic TIs, we here only focus on two very recent breakthroughs: organometallic topological insulators (OTIs) and topological crystalline insulators (TCIs).

Organometallic topological insulators

OTIs, which are composed of covalent organic frameworks with uniformly embedded metal atoms, serve as a new family of TIs. This new concept was proposed by Liu et al. \cite{96}. In verifying this new concept, they designed two organometallic lattices, i.e. 2D triphenyl-lead [Pb(C$_6$H$_3$I)$_3$] lattice and triphenyl-bismuth [Bi(C$_6$H$_3$I)$_3$] lattice, in which a metal atom bonds with three benzene rings with 3-fold rotational symmetry \cite{96}. The lattice is slightly bulked due to the sp$^3$ hybridization of Pb and Bi atoms. The 2D [Pb(C$_6$H$_3$I)$_3$] was found to be a TI with the Fermi level located exactly at the Dirac point. Turning on SOC opens a gap of 8.6 meV at the Dirac point. Replacing Pb with Bi increases the SOC gap to about 43 meV. However, its Dirac point is no longer at the Fermi level, which requires moving the Fermi level into the Dirac-cone gap by additional doping. Incorporating magnetic transition metals into the lattice can lead to the formation of TIs with spin-polarized Dirac cones, which are promising for realizing the quantum anomalous Hall effect. An example is given by the 2D triphenylmanganese [Mn(C$_6$H$_3$I)$_3$] lattice \cite{97}.

Later, Liu et al. identified an experimentally made 2D organometallic framework \cite{98}, which consists of $\pi$-conjugated nickel-bis-dithiolen with a chemical formula Ni$_3$C$_3$I$_2$S$_2$, to be a TI. However, its Dirac point is about 0.5 eV above the Fermi level, which makes the experimental verification difficult.

Topological crystalline insulators

TCIs are a new class of topological materials, which were proposed by Fu \cite{99}. Different from conventional TIs, the metallic surface states in TCIs are protected by the crystal symmetry, such as mirror symmetry, thus the occurrence of topological states requires neither spin–orbit (SO) interaction nor time-reversal symmetry. However, TCIs only have gapless modes in high-symmetry directions or planes, and are vulnerable to certain disorders.

Bulk SnTe is the first TCI that was proposed based on first-principles calculations \cite{100}, and verified by a subsequent experiment \cite{101}. SnTe has metallic surface states with Dirac cones on high-symmetry crystal surfaces such as (001), (110), and (111), which are topologically protected by reflection symmetry of the crystal. TCIs are also predicted in pyrochlore oxides \cite{102}.

The 2D TIs have enhanced carrier contribution from topological surface states compared to bulk ones, thus are superior in observing topology-induced quantum phenomena. Moreover, whether TCIs can exist in reduced dimensions remains unclear. This problem was first settled by Schmidt and Wrasse, who designed a PbSe monolayer, and predicted it to be a potential TCI \cite{103}. Later, Fu et al. made a theoretical study on all the monolayers of XY (X = Ge, Sn, Pb, and Y = S, Se, Te), and found they are all 2D TCIs, where the non-trivial topological phase is resulted from the strong crystal field \cite{104}. Meanwhile, Kindermann also suggested that 2D TCIs can be achieved in graphene
multilayers with certain commensurate interlayer twists [105].

Half semiconductors

Transition-metal dichalcogenides nanosheets

Owing to their excellent electronic and optical properties, 2D transition-metal dichalcogenides (Fig. 5d) have caught much attention in recent years [59]. Unfortunately, most of these materials are non-magnetic. In order to explore their applications in spintronics devices, it is essential to find intrinsic ferromagnetism in these materials. Based on first-principles calculations, monolayer MnO$_2$, synthesized in 2003, was rediscovered to be a 2D ferromagnet with a magnetic moment of 3 $\mu_B$ per Mn atom [106]. The Curie temperature was estimated to be 140 K, which is comparable to the highest $T_C$ value achieved experimentally for Mn-doped GaAs, and can be further increased to 210 K by applying an external strain. The 2D MnO$_2$ is an indirect semiconductor with a band gap of 3.41 eV, with VBM and CBM spin polarized in the same spin channel. Thus, 2D MnO$_2$ is a HSC. However, the relatively big band gap would restrict its further applications. Sun et al. found that by replacing O with S and Se, significantly reduced band gaps of 0.69 and 0.01 eV can be obtained, while maintaining the ferromagnetism and HSC character in the system [107]. Moreover, 2D MnS$_2$ and MnSe$_2$ possess enhanced Curie temperatures of 225 and 250 K, respectively, which can exceed room temperature under strains. More excitingly, a recent theoretical study predicted monolayer V$_5$S$_2$ to be a ferromagnetic HSC with a direct band gap of 1.1 eV [108]. The direct band gap and its suitable gap size, together with the intrinsic ferromagnetism, make 2D V$_5$S$_2$ great potentials in optoelectronics and spintronics applications.

Heusler alloys

In a few cases, Heusler alloys with integer magnetic moments can be magnetic semiconductors. For example, Galanakis et al. proposed the quaternary Heusler compounds CoVXXAl ($X = Ti, Zr, Hf$) as robust ferromagnetic semiconductors [109]. Based on first-principles calculations, these Heusler alloys were predicted to be HSCs with Curie temperatures well above the room temperature. In determining the magnetic properties, the V atoms are considered to play a key role. Later, they found another series of HSCs with zero magnetic moments, i.e. CrVXXAl ($X = Ti, Zr, Hf$), which have even higher Curie temperatures than CoVXXAl [110]. However, the size of exchange splitting in the top of VB is comparatively small.

$CrXe_3$ ($X = Si, Ge$) nanosheets

Bulk CrXe$_3$ ($X = Si, Ge$) are layered crystals with a big interlayer van der Waals gap, which can be easily exfoliated into nanosheets, as predicted by a recent theoretical study [111]. The cleavage energy is comparable to the well-known graphite, directly demonstrating the feasibility of exfoliation in experiment. A rather high in-plane stiffness makes CrXe$_3$ nanosheets form free-standing planar structures. CrXe$_3$ nanosheets are 2D ferromagnetic HSCs with an indirect band gap of 0.95 eV for monolayer CrSiTe$_3$ and 0.88 eV for monolayer CrGeTe$_3$. The gap size can be tuned by changing the thickness of the nanosheets. The Curie temperatures are estimated to be 35.7 K (CrSiTe$_3$) or 57.2 K (CrGeTe$_3$), which can be enhanced to exceed the liquid nitrogen temperature under moderate strains. The magnetic and electronic properties of CrXe$_3$ nanosheets can be further enriched via external operations. For example, by pure electron doping or adsorbing nucleophilic organic molecules, CrXe$_3$ nanosheets change from HSCs to HMFs. Substitution of Mn for Cr may lead to another intrinsic 2D HMF, i.e. MnSiTe$_3$. These results are mostly supported by subsequent studies by other groups, with different Curie temperatures predicted by different spin models [112–115]. Note that, one of the theoretical studies calculated monolayer CrSiTe$_3$ to be an antiferromagnetic semiconductor [113], contrary to other studies. Recently, Xiao et al. have successfully exfoliated bulk CrSiTe$_3$ into few layer nanosheets [115]. Related experimental measurements, combined with detailed theoretical calculations, strongly indicate the ferromagnetism for the CrSiTe$_3$ nanosheets, although absolute proof of the magnetization is still lack. As evidenced by the clear change in resistivity, the Curie temperature of monolayer CrSiTe$_3$ is likely to be around 80 K. Followed by the CrSiTe$_3$ and CrGeTe$_3$, a hypothetical 2D CrSnTe$_3$ has also been proposed [114], which is both mechanically and dynamically stable, and exhibits a much higher Curie temperature than CrSiTe$_3$ and CrGeTe$_3$.

Single layer of chromium trihalides CrX$_3$

($X = F, Cl, Br, I$)

Bulk chromium trihalides CrX$_3$ ($X = F, Cl, Br, I$) are another class of layered crystals. Zhang et al. pointed out that through exfoliation, single layer of CrX$_3$ can be obtained [116]. The estimated cleavage energy is even smaller than that of graphite. First-principles calculations revealed that all the monolayer CrX$_3$ are ferromagnetic HSCs with indirect band gaps ranging from 1.5 to 4.7 eV. The band gaps and absorption edges of CrBr$_3$ and CrI$_3$ are in the
visible light region, making them particularly interesting for optoelectronics. The Curie temperatures were estimated up to 95 K, which can be further enhanced by external strains. Because of reduced dimensionality, monolayer CrX₃ present significantly large magnetic anisotropy compared to commonly used ferromagnetic materials, which are promising for low-dimensional magnetoelectronic applications.

### Spin gapless semiconductors

**Heusler alloys**

Heusler alloys play a key role in the development of SGS. The inverse Heusler alloy Mn₂CoAl is the first SGS material that has been verified by experiment [30]. Its success stimulates intensive search of SGS materials in various Heusler alloys. Heusler alloys have a large number of family members, usually high Curie temperatures, and are compatible with current semiconductor technology. Note that the occurrence of SGS is not accompanied by a general rule and it is materials specific. In the inverse Heusler alloy family, Galanakis et al. identified another five potential SGS materials by searching all the inverse Heusler alloys X₂YZ where X = Sc, Ti, V, Cr or Mn, Z = Al, Si or As and Y is a transition metal ranging from Ti to Zn [117]. In the quaternary Heusler alloy family, they also found eight potential SGSs after a systematical study [53]. Theoretical predictions and experimental verifications on the SGS behavior of two quaternary Heusler alloys CoFeMnSi and CoFeCrGa have been made recently [118,119].

**Graphene and graphitic nanostructures**

Through chemical or physical modifications, graphene and its analogous systems provide another possibility to explore SGS materials. Based on first-principles calculations, Chen et al. found that by nitrogen doping, zigzag graphene nanoribbons (ZGNRs) can be tuned into SGS (Fig. 5c) [120]. For example, single N atom substitution of the edge carbon atom, which is energetically favored, removes the spin polarization of the doped edge and makes the ZGNR an SGS. Similar results were predicted for N-doped silicene nanoribbons [121]. By embedding Au atoms in the center or edge sites of ZGNR, the SGS property also occurs [122]. In BN nanoribbons, by engineering B or N vacancies, SGSs can also be obtained [123]. Such an SGS property is formed by the spin-up and spin-down impurity states near the Fermi level, which is different from that of N-doped ZGNR. Note that in these systems, the occurrence of SGS is very sensitive to the dopant or vacancy sites, and the distance between them, which requires a precise control of modifications in experiment. Thus, it is necessary to find intrinsic SGS in carbon-based systems. Zhao et al. designed a honeycomb lattice of tri-s-triazine (C₃N₆) units, which shows an intrinsic SGS property with linear energy dispersion, while the hybrid honeycomb lattice of the C₃N₆ and s-triazine (C₃N₃) units is an SGS with parabolic energy dispersion [124].

### Bipolar magnetic semiconductors

**Graphene and graphitic nanostructures**

(Figs 7a–c)

The first proposed BMS materials are semihydrogenated carbon nanotubes [31], where semihydrogenation refers to the hydrogenation of carbon atoms in only one sublattice. Hydrogenation, as a simple means of chemical functionalization, has been widely applied to low-dimensional materials to tune their electronic, magnetic, and optical properties. For carbon nanotubes, semihydrogenation destroys the extensive π bond and makes the π electrons of the carbon atoms in the other sublattice localized and spin polarized. First-principles calculations predicted that all the armchair-type semihydrogenated carbon nanotubes, and zigzag-type ones with big diameters, are ferromagnetic BMSs. Further spin transport simulations confirmed the concept of electrical control of spin polarization in BMSs. When the diameters of the semihydrogenated carbon nanotubes become infinity, a semihydrogenated graphene is obtained, which was also shown as a ferromagnetic BMS material [125]. Similar results were reported for semihydrogenated SiC and BAs nanosheets [126–128]. Except semihydrogenation, asymmetric edge hydrogenation is another efficient method to get BMSs from nanoribbon systems. For example, ZGNRs with one edge fully hydrogenated while the other edge partially hydrogenated were predicted to be ferromagnetic BMSs [129,130]. A similar case can be found for silicene nanoribbons [131].

Recently, it has been shown by Liu et al. that an intrinsic ferromagnetic BMS character is attainable in graphene nanoribbons with sawtooth edges, where spin-up electrons are localized at one edge while spin-down holes at the opposite edge [132]. The BMS behavior is robust against edge disorder and can be tuned by electric field or strain. A followed work showed that the silicene nanoribbons with sawtooth edges also exhibit similar properties [133]. Moreover, they are more stable than silicene nanoribbons with zigzag edges.
Figure 7. Some materials that have been predicted as BMSs so far: (a) semihydrogenated carbon nanotubes (Adapted from Ref. [31] with permission. Copyright 2012 Royal Society of Chemistry.), (b) semihydrogenated bilayer SiC (Reprinted from Ref. [127] with permission. Copyright 2012 Royal Society of Chemistry.), (c) silicon nanoribbons with asymmetric edge hydrogenation (Reprinted from Ref. [131] with permission. Copyright 2013 American Institute of Physics.), (d) ZrCuSiAs-type La(Mn_{0.5}Zn_{0.5})AsO alloy (Reprinted from Ref. [136] with permission. Copyright 2013 Royal Society of Chemistry.), (e) MnPSe$_3$ nanosheets (Reprinted from Ref. [33] with permission. Copyright 2014 American Physical Society.), and (f) FeVTiSi Heusler alloy (Adapted from Ref. [139] with permission. Copyright 2015 Royal Society of Chemistry.).

ZrCuSiAs-type compounds (Fig. 7d)
ZrCuSiAs-type compounds incorporate a large number of family members, including the famous LaFeAsO superconductor [134]. They crystallize in a double-layered structure with the first layer composed of transition metals coordinated tetrahedrally by heavy chalcogen or pnictogen atoms, while the second layer constructed by oxygen or fluorine atoms coordinated tetrahedrally by rare earth or alkaline earth metals. By altering the four composite elements, the properties of ZrCuSiAs-type compounds can be tuned.

Bannikov and Ivanovskii made the first effort to search BMS in this type of compounds. They found that by doping magnetic ions such as Mn$^{2+}$ in a non-magnetic semiconductor YZnAsO, a BMS property can be gained [135]. Based on LaMnAsO and LaZnAsO, Li et al. designed a novel hypothetical La(Mn$_{0.5}$Zn$_{0.5}$)AsO alloy [136], which is a BMS at the ferromagnetic state, but an antiferromagnetic semiconductor at the ground state. They suggested that electron and hole doping can induce the transition from antiferromagnetic to ferromagnetic, thus realizing the BMS property. It is expected that the large number of ZrCuSiAs-type compounds provide a fertile soil for searching BMS materials.

MnPSe$_3$ nanosheets (Fig. 7e)
Free-standing MnPSe$_3$ nanosheets can be exfoliated from its bulk crystal, which was firstly proposed by Li et al. [33] and has been realized in a recent experiment [34]. The 2D MnPSe$_3$ is an antiferromagnetic semiconductor at its ground state, which can be tuned into a ferromagnetic half metal under both electron and hole doping. Moreover, the spin-polarization directions of 2D half-metallic MnPSe$_3$ are opposite for electron and hole doping, which can be controlled by applying an external voltage gate. This property is similar to that of La(Mn$_{0.5}$Zn$_{0.5}$)AsO alloy, but it seems much easier to achieve in 2D MnPSe$_3$ since carrier doping in 2D systems can reach a very high level [137,138].

Heusler alloys FeVXSi (X = Ti, Zr) (Fig. 7f)
Heusler alloys provide the possibility to explore BMS materials with room-temperature magnetic ordering. Based on first-principles calculations, Zhang et al. suggested the quaternary Heusler alloy FeVTiSi to be a potential ferromagnetic BMS with the Curie temperature well above the room temperature [139]. The BMS character can be further tuned by replacing Ti with Zr. Note that in an early paper, FeVTiSi was calculated to be an SGS [53]. However, the calculations therein were based on GGA functional, which tends to give a much reduced energy gap compared with the experiment. This indicates that some of the previously predicted SGS materials may actually be BMSs when using a more accurate calculation method.

Asymmetric antiferromagnetic semiconductors
The search of AAFMSs can be done in systems that contain multiple magnetic sublattices, such as double perovskites, Heusler alloys, chalcopyrites, and ZrCuSiAs-type compounds. Besides, the HMAFM materials provide another platform to get AAFMSs. By lattice distortion, chemical or physical doping, or just changing the transition-metal pairs, HMAFMs may be transformed into AAFMSs.

Li et al. designed a series of AAFMSs in double perovskites $A_3$CrMO$_6$ (A = Ca, Sr, Ba, and M = Ru, Os) [35], where Cr is in +3 valence state and M in +5 valence state. Both Cr$^{3+}$ and M$^{5+}$ ions carry a spin magnetic moment of $\mu_B$, which prefer to be antiferromagnetically coupled with each other. The Néel temperatures were estimated to be as high
as 500 K. Electronic structures calculations revealed that the $\text{A}_2\text{CrRuO}_6$ are HSCs while $\text{A}_2\text{CrOsO}_6$ are BMSs. Chemical doping of these semiconductors can induce either n-type or p-type conductivity with a high spin polarization at the Fermi level.

**ANTIFERROMAGNETIC SPINTRONICS**

Up to now, the main active components of spintronics devices are ferromagnets, which are well understood and can be handled easily. However, to continuously reduce the device size would be limited, since the parasitic magnetic field of ferromagnets can interfere with each other. A possible solution is to replace used ferromagnets with antiferromagnets. According to related theoretical studies, the phenomena occurred in ferromagnetic systems such as spin transfer torque, spin pumping, GMR, and tunnel anisotropic magnetoresistance (TAMR) are also inherent to antiferromagnetic systems regardless of their different magnetic structures [140–143]. Moreover, antiferromagnets possess at least three potential advantages over ferromagnets. The first advantage is that antiferromagnets are more common in nature and significantly abundant than ferromagnets. Moreover, by selective design, antiferromagnets can be made to be metals, half metals, HSC, SGS, BMS, and so on, as discussed in the above sections. Second, due to zero or nearly zero magnetization, antiferromagnets do not create redundant magnetic fields and interact weakly with each other, which is particularly important at nanoscale. Last, the switching between different states of antiferromagnets tends to be several orders faster than ferromagnets [144]. Because of these reasons, antiferromagnets are very promising in developing ultrafast and ultrahigh-density spintronics devices. The main obstacle for antiferromagnetic spintronics is that compared to ferromagnets, antiferromagnets are usually more complex in behavior, which have not been fully understood yet. Furthermore, the requirement of device quality may be significantly stringent for antiferromagnetic spintronics.

To date, researches are devoted to studying the interaction of antiferromagnets with spin currents, formulating new concepts and models, and developing antiferromagnetic metals for TAMR.

TAMR refers to the variation of resistance across a tunnel barrier, as a function of the angle between the directions of the magnetic moments and that of the current. For application in TAMR, antiferromagnetic metals should have a high magnetic ordering temperature and large SOC, i.e. strong magnetic anisotropy.

Based on first-principles calculations, Jungwirth et al. studied the magnetic anisotropy phenomena in bimetallic antiferromagnets $\text{Mn}_2\text{Au}$ and $\text{MnIr}$ [145], which possess a very high Néel temperature of about 1300 and 1200 K, respectively [146,147]. They found that the ground-state energy, chemical potential, and electronic density of states in these two alloys are strongly dependent on the orientation of magnetic moments, which can be tuned by applying a small strain without involving ferromagnets. Another example is the tetragonal phase CuMnAs [148], which is a room-temperature antiferromagnetic semimetal with its in-plane lattice constant well matched to Si.

**SUMMARY AND PERSPECTIVES**

Spintronics materials incorporate a huge number of magnetic materials, including magnetic metals, TIs, and magnetic semiconductors. To overcome the challenges facing spintronics, several new conceptual materials have emerged, such as half metals, SGSs, BMSs, and AAFMSs. The proposal of these materials is primarily based on first-principles calculations, and some of them have been verified by subsequent experiments, while others still left as theoretical models. Because of the abundance of family members and magnetoelectronic properties, double perovskites, Heusler alloys, transition-metal chalcogenides and pnictides, as well as graphene and graphitic nanostructures form fertile soils for the design of spintronics materials.

Spintronics still has a long way to go before its wide application in real life. Further development of spintronics is expected to focus on the following areas:

1. Proposing new concepts and spintronics materials. Up to now, most spintronics materials are featured by only one specific property or function. Nevertheless, it is possible to create a magnetic material with multifunctionality. This is not only interesting for fundamental research but also for fabricating multifunctional spintronics devices.

2. Seeking more candidate compounds for different classes of spintronics materials. For example, continuous efforts are needed to search for more SGSs, BMSs, and AAFMSs, since their family members are still much limited. In this respect, the Materials Genome Initiative serves as a good opportunity. Meanwhile, recently developed crystal structure search methods such as USPEX [149] and CALYPSO [150] provide us with very powerful tools.
3. Developing spintronics materials that can work at room temperature. To do this, efforts should be devoted to obtaining half metals with high Curie temperature and wide half metallic gap, TIs with sizable SOC gap, and magnetic semiconductors with room temperature magnetic ordering and large spin polarization.

4. Designing low-dimensional spintronics materials to construct spintronics devices at nanoscale. This is particularly important for fabricating devices with high integration density and speed.

5. Understanding and engineering the interface between magnetic metals and semiconductors. In an ideal spintronic circuit, spin current will cross the interface without losing its polarization. How to realize such an Ohmic contact for spins remains a challenge. Meanwhile, control of the magnetic interaction between two ferromagnetic components in the integrated circuit is also important.

6. Exploring antiferromagnetic spintronics. Lots of works are still needed to improve the understanding and comprehension of antiferromagnetic spintronics both from theoretical and experimental aspects. Also, developing novel device models and practical antiferromagnetic materials is required.

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