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二维材料理论与计算专辑 评 述
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二维铁磁材料的理论模拟与设计

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摘要 二维本征磁性材料具有不同于体相材料的奇异物理性质, 为低维自旋电子学的发展提供了理想的研究平台. 传统开发新材料的方法是试错法, 具有研发周期长、成本高等固有缺陷. 近年来, 随着计算机算力的快速提升, 基于密度泛函理论的第一性原理计算方法为新型本征铁磁材料的设计和材料磁学性质的研究提供了一种十分有效的手段. 本文综述了近年来在二维本征铁磁材料方面的研究进展, 特别是强调了第一性原理计算在铁磁材料探索和制备方面发挥的重要作用. 最后, 展望了二维铁磁材料未来的发展和面临的挑战.

关键词 二维材料, 铁磁材料, 第一性原理, 磁各向异性

电子自旋作为信息载体具有非易失性、能耗低和交换速度快的优点, 自旋电子器件也是未来信息技术的发展方向, 引起了全世界的广泛关注[1~6]. 早期二维磁体的制备主要是通过外延生长等特殊设计的方法, 精细控制层对层生长, 将三维非范德华磁性材料的厚度减小到数个原子层, 比如体心立方相的铁晶体可以在合适的半导体表面上(MgO(001)[7]、GaAs(001)[8]、GaAs(110)[9,10]、ZnSe[11,12]等)生长成几个原子厚度的薄膜单晶. 然而, 该方法很难精准控制衬底与晶格之间的界面条件, 导致外延磁覆层的晶格容易发生应变和重构. 近年来, 二维范德华材料展现出许多新颖的物理化学性质, 是未来信息、能源、医学等领域先进技术的一个优良载体. 正如石墨烯、过渡金属二硫族化合物和二维黑磷的发现彻底改变了凝聚态物理领域和材料工程领域一样, 二维范德华层状铁磁材料的发现有望为自旋电子学开辟新的篇章[13~15]. 事实上, 二维铁磁材料已经被研究了数十年, 直到最近才在实验上有所突破, 这主要得益于理论计算和实验技术的有效结合. 令人兴奋的是, 研究者们成功从范德华层状块体剥离出了单层或少数层CrX_3(X = Cl, Br, I)[1,16,17]、单层Fe_3GeTe_2[18,19]和双层$CrGeTe_3$[2], 并且它们都具有长程铁磁序. 这一发现推动了对新型低维纳米铁磁材料的研究, 打开了范德华二维本征铁磁材料的大门. 与传统的磁性薄膜相比, 二维范德华磁性材料与衬底的相互作用比较弱, 可以很容易地通过外加电场或化学修饰等方法对自旋方向进行探测和调控[6]. 目前人们已经探索和设计出了许多二维铁磁材料, 包括金属、半金属以及半导体, 但其种类和数量依然稀少, 仍需要我们投入更多的精力去研究.

材料学科的发展长期依赖于实验的“试错法”, 采用经验指导实验, 往往缺少明确的目标和清晰的指导方针, 面临着研发时间长和成本高等固有问题. 如何减少研发成本, 加快新材料的研发过程, 尤其是在没有实验的时候就能预测出材料的结构和性能, 是新材料研

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发需要解决的重要问题. 从特定性能出发“逆向”设计新材料也是材料科学研究的终极目标. 随着计算机算力的提升和理论计算方法的快速发展, 计算模拟已经成为探索新材料潜在用途重要的第一步. 计算模拟可以通过对数据的归纳与分析, 获得实验可观测的物理量; 可以透过表象探索结构与性能之间的关系来揭示其隐藏的机理; 还可以设计出材料可能的合成途径, 大大节约实验成本. 截至目前, 实验已经证实了许多理论上预测的有趣案例: 例如二维硼烯和碲烯的生长过程[20~22]、二维硒化锡的热电性质[23]、二维碲化锡的铁电性[24,25]以及黑磷的高载流子迁移率[26]等. 这些实例展示了理论计算方法的准确性及其在二维材料领域强大的探索能力. 与其他计算方法相比, 第一原理方法是设计新材料时使用最广泛的工具之一. 例如, 最常见的广义梯度近似(generalized gradient approximation, GGA)[27]下PBE(Perdew-Burke-Ernzerhof)[28]泛函只需要几个基本物理参数和原子位置坐标就可以模拟出材料基本的物理化学性质. 此方法的价值主要在于它能以极小的成本预测和设计出具有优异性能的新材料, 在很大程度上可以代替昂贵且耗时的实验测试. 事实上, 二维铁磁材料的快速发展确实得益于理论上的理性设计与模拟. 例如, 超薄的VSe_2在理论上首先被认为具有本征的铁磁性, 随后被实验证实[29~32]. 双层$CrGeTe_3$[33]、单层CrI_3[34]和单层Fe_3GeTe_2[35]也是先被理论计算预测具有铁磁性且易于实验剥离, 随后它们在实验上都得到了证实[1,2,18,19]. 这些例子显示了第一性原理计算在预测和设计自旋电子新材料方面的强大作用, 也说明了利用此方法去探索新材料是可行有效的. 就目前而言, 实验研究与计算模拟的结合已经成为材料研究的新风向. 理论与实验相辅相成, 是加快新材料研发的捷径.

本文综述了近年来二维铁磁材料的最新进展、当前挑战和未来前景. 希望本文能展现出第一性原理计算在促进二维铁磁材料研究中的重要作用. 为此, 首先给出了在有限温度下二维空间中存在铁磁序的根本原因; 然后, 分别以二维的CrI_3、$CrGe_2Te_3$、Fe_3GeTe_2和$FeCl_2$为例, 概述了几种二维铁磁半导体、金属和半金属的发现过程及各自的磁学性质; 最后, 介绍了二维铁磁材料研究目前存在的问题, 并提出了进一步可能的发展方向. 当然, 本文不能涵盖所有二维铁磁材料, 读者也可以参考其他综述和文献以获取更多的低维铁磁材料信息[36~44].

1 磁各向异性

根据Mermin-Wagner定理, 在二维各向同性海森堡模型中, 非零温下的热涨落导致磁振子都处于激发态, 因而无法组成自旋有序相[45]. 对于二维各向同性的海森堡铁磁体来说, 由于自旋波的色散关系中磁振子禁带的缺失、玻色爱因斯坦凝聚的缺失以及零能量下存在的较高磁振子态密度, 因此在较低的温度下便可激发出大量磁振子, 从而扰乱磁性, 导致长程自旋磁有序的崩塌(图1(a)). 单轴磁晶各向异性(uniaxial magnetic

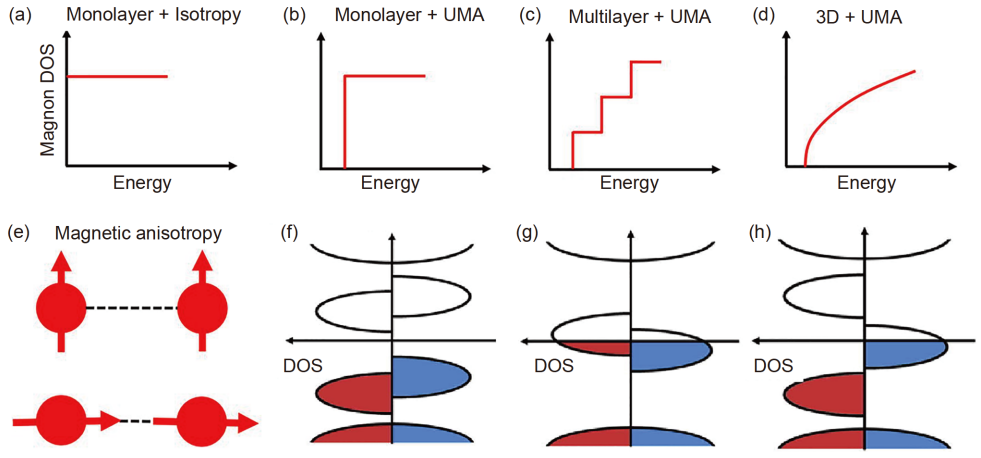

图 1 (网络版彩色)不同维度铁磁体的基本物理参数及3种类型的铁磁体. (a)~(d) 不同尺寸下铁磁体中的磁振子态密度; (e) 磁各向异性[6]. Copyright © 2019, AAAS. (f)~(h) 3种类型铁磁半导体、金属和半金属材料自旋极化态密度示意图[37]. Copyright © 2018, Elsevier

Figure 1 (Color online) Fundamental physical parameters in ferromagnets of different dimensionalities and three types of ferromagnetic materials. (a)–(d) Spin wave excitations in ferromagnets of different dimensionalities; (e) magnetic anisotropy[6]. Copyright © 2019, AAAS. (f)–(h) Schematic density of states for three types of ferromagnetic semiconductor, metal and half-metal[37]. Copyright © 2018, Elsevier

anisotropy, UMA)可以打开磁振子激发间隙, 从而可以有效地抵抗磁振子的热扰动(图1(b)). 这使得电子自旋磁矩满足的海森堡模型中多了一项, 破坏了海森堡哈密顿量的连续旋转对称性, 导致了有限的居里温度(Curie temperature, T_C) [6]. 随着磁性材料从二维演化到三维, 磁振子的态密度已从阶跃函数变为逐渐增加的函数, 最后自发形成自旋波激发间隙(图1(c), (d)). 因此, 磁各向异性不是三维系统中长程磁有序的必要条件, 但它却是二维长程磁性存在的先决条件.

磁各向异性是实现二维铁磁材料的关键, 它不仅影响磁性和自旋传输特性, 而且在二维空间中可以稳定磁序[46]. 磁各向异性(图1(e))可以通过磁各向异性能(magnetic anisotropy energy, MAE)来表征, 它与磁数据存储的热稳定性密切相关. MAE被定义为易磁化方向(最低能量)和难磁化方向(最高能量)之间的能量差[47]. 目前, MAE的微观机制主要有以下几种: (1) 磁偶极相互作用. 经典的磁偶极作用只对非立方晶体能引起各向异性, 它是形状各向异性的起源. (2) 各向异性交换作用, 主要来自自旋-轨道作用对交换作用的影响, 主要存在于某些稀土离子及低对称化合物中. (3) 单离子各向异性为晶体电场和轨道-自旋作用的联合效应, 它使单个离子的能级呈现各向异性. (4) 巡游电子各向异性. 主要来自轨道-自旋作用对能带的影响, 大多适用于3*d*金属及合金中, 其他因素对MAE的贡献较小[48]. 然而, MAE的微观起源仍未有定论, 还需进一步的深入研究. 同时, 目前的二维铁磁材料通常具有较小的MAE(低于1 meV), 这在实验上也很难测量, 因此需要更有效的策略来增强MAE或设计出具有较大MAE的新型二维铁磁材料.

2 二维磁性的预测

磁性通常源自部分填充的*d*或*f*轨道中的不成对电子. 二维铁磁材料是研究新奇物理现象以及自旋电子学器件应用的重要基础. 二维铁磁材料的理论研究要远早于实验, 多种二维铁磁材料被理论预言, 显示出多样的磁学性质. 根据电子结构特性的不同, 铁磁材料可以分为三类: 铁磁半导体(ferromagnetic semiconductor, FMS)、铁磁金属(ferromagnetic metal, FMM)和铁磁半金属(ferromagnetic half-metal, FHM). 根据易磁化方向的不同, 铁磁材料一般可以分为海森堡(Heisenberg)磁体、XY磁体和伊辛(Ising)磁体(图2(a)). 海森堡铁磁体没有磁各向异性, 各个方向的磁矩是等效的; XY铁磁

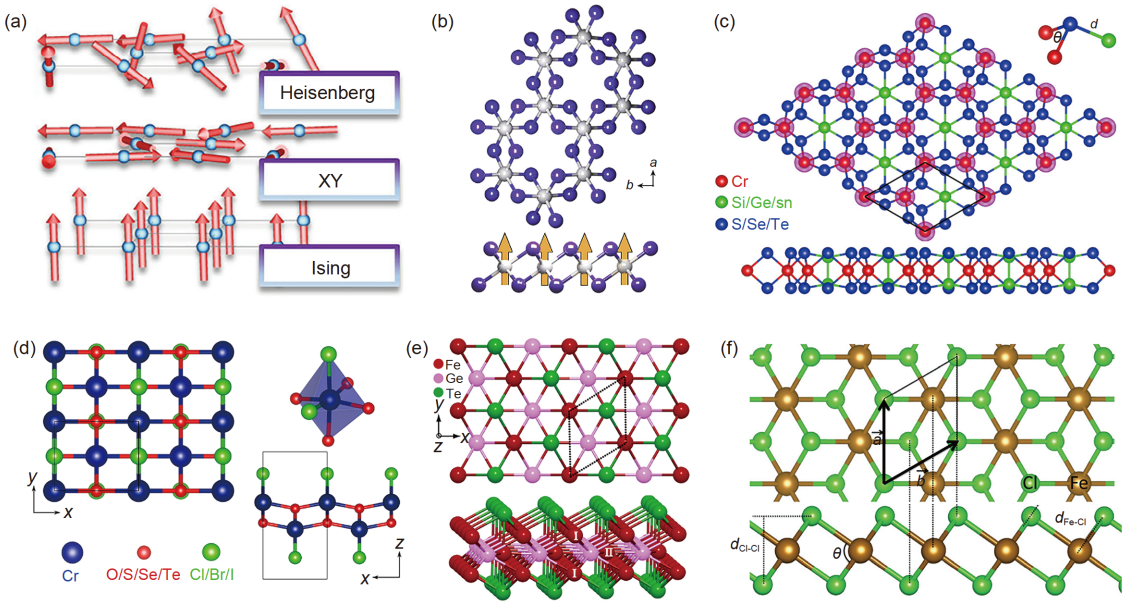

图 2 (网络版彩色)磁各向异性的自旋对称性及几种典型晶体结构. (a) 海森堡模型、XY模型和伊辛模型中自旋的方向[36]. Copyright © 2020, John Wiley & Sons. CrX_3(X= Cl, Br, I)单层(b)、$CrMX_3$(M = Si, Ge; X = S, Se, Te)单层(c)、CrCX(X = Cl, Br, I; C = O, S, Se, Te)单层(d)、Fe_3GeTe_2单层(e)和$FeCl_2$单层(f)结构俯视图和侧视图

Figure 2 (Color online) Spin symmetry of magnetic anisotropy and several typical crystal structures. (a) Isotropic Heisenberg model, XY model, and Ising model, respectively[36]. Copyright © 2020, John Wiley & Sons. The top and side views of CrX_3 (X= Cl, Br, I) (b), $CrMX_3$ (M = Si, Ge; X = S, Se, Te) (c), CrCX (X = Cl, Br, I; C = O, S, Se, Te) (d), Fe_3GeTe_2 (e), and $FeCl_2$ (f) monolayers

体具有易磁化平面，自旋可在整个二维平面内自由旋转; 伊辛铁磁体具有垂直于平面的易磁化轴, 很容易受外界磁场的控制.

2.1 铬基铁磁半导体

FMS(图1(f))结合了半导体和磁体的优点和性能, 是自旋电子学中最有应用前景的候选材料之一，可用于自旋注入、自旋操纵和自旋检测[40]. FMS前期的研究经历了浓磁半导体和稀磁半导体两个阶段. 浓磁半导体是自然界中存在的本征体相铁磁半导体，但它的缺点是无法与主流半导体相兼容且居里温度较低. 研究者尝试了各种手段去调控，但其性能并没有显著的提升. 于是他们把目光转移到了稀磁半导体. 稀磁半导体是将磁性原子掺杂于半导体中，其居里温度虽然较高，但存在可重复性差、掺杂浓度低、自旋极化低和容易形成团簇等难以解决的问题. 半导体和铁磁性的不兼容导致了目前本征铁磁半导体在自然界中非常罕见, 更难以找到室温铁磁半导体. 范德华二维铁磁材料的兴起为铁磁材料研究开辟了新方向，这类材料具有层数依赖特性, 对光、电刺激更敏感, 具有极大调控的自由度, 应用前景十分广阔.

最近实验上成功合成了二维CrI_3单层, 它是典型的二维FMS之一(图2(b)). 它的发现过程说明了第一性原理计算在预测和设计新材料方面的强大功能，并展示了实验与理论之间的密切联系. 实验测定的层状范德华块体CrI_3的T_C是61 K，具有较强的单轴磁各向异性, 说明它是伊辛铁磁性[49]. 很自然地, 人们猜想是否可以像石墨烯一样采用机械剥离的方法去得到原子层厚度的CrI_3铁磁材料. 理论计算研究发现CrI_3是稳定的二维FMS，且很容易从层状块体中机械剥离，其剥离能($0.29\ J\ m^{-2}$)比实验上石墨烯($0.36\ J\ m^{-2}$)的还小. 计算得到CrI_3具有较大的单轴磁各向异性，每个Cr原子具有3个玻尔磁子. 基于海森堡模型的蒙特卡洛模拟结果显示，CrI_3单层的T_C是95 K[50]. 其他蒙特卡洛模拟工作也表明CrI_3单层的T_C为107 K，并通过空穴掺杂可以进一步提高到293 K[33]. 令人兴奋的是, 两年后, CrI_3单层成功地从其层状块体中剥离，并通过磁光克尔技术首次在单层体系中确认了固有长程铁磁序(图3(a))，这为自旋电子学打开了新的大门[1]. CrI_3单层T_C的测量值是45 K, 比块体材料略低, 说明块体层间存在较弱的铁磁耦合. 尽管理论计算的T_C值略高于实验值, 第一性原理计算的方法仍然显示出了其强大的预测能力，大大节

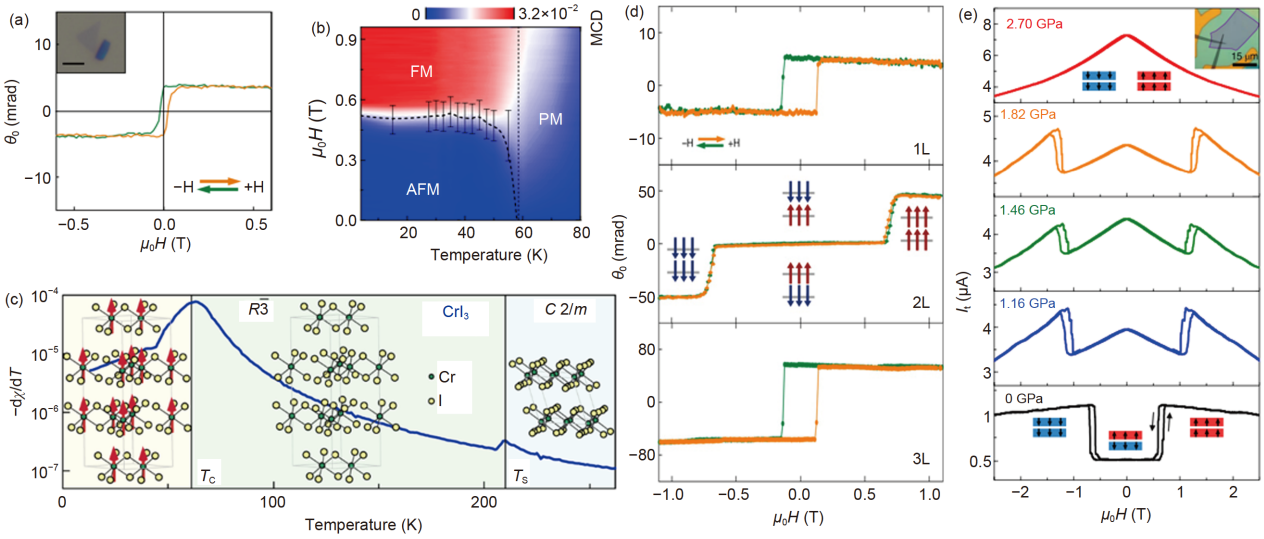

图 3 (网络版彩色)不同外部作用下CrI_3相关的性质. (a) CrI_3单层的磁光克尔(magneto-optic Kerr effect)信号[1]. Copyright © 2017, Springer Nature. (b) 双层CrI_3的磁圆二色谱与磁场和温度(*H-T*)变化关系[51]. Copyright © 2018, Springer Nature. (c) 块体CrI_3的晶体结构随温度的变化[49]. Copyright © 2015, American Chemical Society. (d) 单层、双层和三层CrI_3薄片的磁序[1]. (e) 不同压力下的隧穿电流I_t与磁场H的关系[52]. Copyright © 2019, Springer Nature

Figure 3 (Color online) Properties of CrI_3 under different external actions. (a) Polar magneto-optic Kerr effect signal for a CrI_3 monolayer[1]. Copyright © 2017, Springer Nature. (b) *H-T* phase diagram of the magnetic order in bilayer CrI_3 determined from the magnitude of the magnetic circular dichroism[51]. Copyright © 2018, Springer Nature. (c) The crystal structures of bulk CrI_3 at different temperatures[49]. Copyright © 2015, American Chemical Society. (d) Layer-dependent magnetic ordering in atomically-thin CrI_3[1]. (e) Tunnelling current I_t, versus magnetic field H, at a series of pressures[52]. Copyright © 2019, Springer Nature

约了实验探索的成本.

对于CrI_3双层, 第一性原理计算表明它是层间反铁磁耦合; 进一步的研究表明, 其层间堆叠方式决定了磁性的基态性质, 该结论最近已被实验证实[53~55]. 同时, CrI_3双层的磁基态可以在电场(图3(b))[51]和压力(图3(e))[52]的调控下从反铁磁态转换为铁磁态. 此外, 最近的理论工作表明, 块体CrI_3在约200 K时经历了从高温单斜相到低温菱面体相的转变(图3(c)), 但这种转变在少数层CrI_3中却被抑制了[53,56,57], 该结论也得到了实验的证实(图3(d))[58,59]. 此外, 同构的范德华层状$CrBr_3$和$CrCl_3$也是先在理论上被预测具有铁磁有序性, 随后实验证实了$CrBr_3$单层[17]和$CrCl_3$双层[16]的晶格结构和磁性性质[60].

另一类典型的二维FMS是$CrMX_3$(M=Si, Ge; X=S, Se, Te, 图2(c)). 2014年, 理论计算表明二维$CrXTe_3$(X=Si, Ge)是本征的FMS, 且可以通过剥离其层状块体得到. 基于经典的海森堡模型进行蒙特卡洛模拟, 它们的T_C分别是35.7 K($CrSiTe_3$单层, 图4(a))和57.2 K($CrGeTe_3$单层, 图4(b))[34]. Sivadas等人[64]的研究表明$CrSiTe_3$单层是具有锯齿形自旋纹理的反铁磁. 随后, Zhuang等人[61]通过杂化密度泛函方法(Heyd-Scuseria-Ernzerhof screened hybrid functional, HSE06)研究了$CrSnTe_3$单层, 结果表明它是本征的FMS, 且其蒙特卡洛模拟的T_C理论值约170 K, 高于$CrGeTe_3$单层(130 K)和$CrSiTe_3$(90 K)单层(图4(c)). 不久, Gong等人[2]通过磁光克尔技术也证实了二维$CrGeTe_3$双层中固有的长程铁磁序, 并且测得双层$CrGeTe_3$的T_C约30 K(图4(d)). 此外, 施加一个小磁场即可实现对转变温度的调控, 也会导致更大的有效磁晶各向异性, 打开更大的自旋波激发间隙. 这与块体材料转变温度对磁场的不敏感性形成鲜明对比. 尽管$CrGeTe_3$单层仍未被实验证实, 第一原理方法仍在推动新型二维铁磁材料发现和指导实验中发挥了重要作用.

此外, 利用第一性原理方法, 另外几种Cr基半导体单层也被预测具有本征铁磁性, 且具有较大自旋极化和较高的T_C. 二维本征铁磁半导体CrOCl和CrOBr单层被认为可以从其层状反铁磁块体中机械剥离, 其基于伊辛模型的T_C理论值分别高达为160和129 K(图4(e))[62]. 具有同种结构的CrOF也被预测为本征的FMS, 它的T_C为150 K; 在空穴掺杂下, 其T_C可以升高到410 K[65]. 本课题组[66]也研究了FMS CrSX(X=Cl, Br, I)单层, 计算结果表明它们具有高的空穴迁移率(10^3 cm^2 V^{-1} s^{-1})和较高的居里温度(150~170 K). Wang等人[63]进一步研究了CrCX(X=Cl, Br, I; C=S, Se, Te)单层的铁磁性能, 发现CrSeBr的有效质量和载流子迁移率表现出明显的各向异性(图4(f), (g)). $Cr_2I_3X_3$(X=Br, Cl)单层也是一种间接带隙半导体, 具有本征的铁磁性[67]. Cr_2O_3单层在双轴拉伸应变下具有较大的面外MAE, 其基于伊辛模型的T_C理论值高达332 K[68]. 值得注意的是, 最近对范德华层状块体CrOCl和CrSBr进行的重复实验研究表明, 它们在空气中能够稳定存在, 且剥离成原子层厚度的可能性很大[69,70]. 尽管理论工作的迅速发展已产生了许多非常重要的结果, 但是目前报道的理论和实验上的二维FMS仍然很少, 在搜索或设计新型铁磁半导体材料方面仍需付出更多的努力.

2.2 铁基铁磁金属

对于铁磁金属(FMM, 图1(g))而言, 其自旋向上和自旋向下的通道都是导通的[37]. 由于电荷载流子驱动的强交换作用, FMM通常具有更高的T_C[46]. 其中, Fe_3GeTe_2单层(图2(e))最近受到了广泛的关注, 因为它是唯一的已在自旋电子器件中用作铁磁电极的二维铁磁单层[71~73]. 通过高分辨率透射电子显微镜的研究, 范德华层状块体Fe_3GeTe_2在低于230 K时显示出比较强的铁磁性[74]. 利用第一性原理计算和角分辨光电子能谱技术, 人们对块体Fe_3GeTe_2的金属性进行了测定, 观察到3*d*电子中的重费米子态[75]. 进一步理论和实验的研究表明, 块体Fe_3GeTe_2是具有强关联性的铁磁金属[76]. 理论研究表明Fe_3GeTe_2单层是一种潜在的二维FMM, 可以很容易地从其范德华层状块体中剥离, 并且具有较大的单轴MAE(920 μeV Fe^{-1})[35]. 两年后, Fe_3GeTe_2单层被成功剥离出来, 其铁磁性也得到了证实(图5(b)). 但是它的T_C从块体的207 K大幅下降到单层的130 K, 表明其磁性具有较强的层数依赖关系(图5(c)), 也说明了层与层之间较强的范德华作用的存在[18]. 有趣的是, 较小的栅极电压可以将Fe_3GeTe_2单层的T_C升高至室温(图5(d)), 高于块体材料的T_C[19]. 此外, 通过改变脉冲的密度, 可以在Fe_3GeTe_2中实现最高的畴壁密度状态, 此性质在高密度存储器件中具有应用潜力[78].

最新的由理论设计和实验验证的铁基范德华层状材料Fe_4GeTe_2也显示出了大磁化强度、高电导率和近室温铁磁有序的特点, 其性质在剥离成7层的薄层中也能很好的保留[79]. 此外, 范德华层状材料Fe_5GeTe_2也在

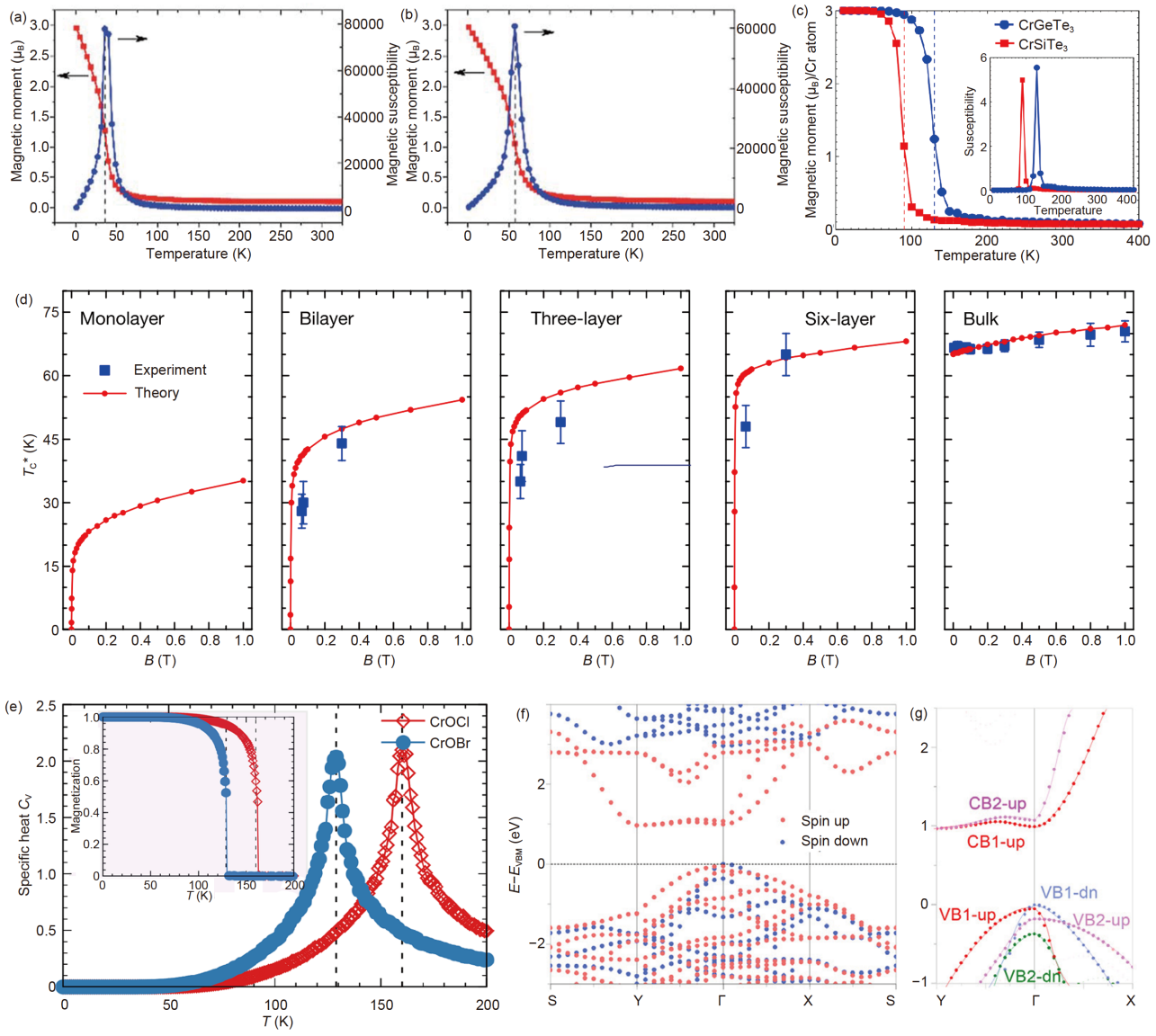

图 4 (网络版彩色)二维Cr基铁磁半导体. 单层$CrSiTe_3$(a)和$CrGeTe_3$(b)磁矩(方形)和磁化率(圆圈)随温度的变化[34]. Copyright © 2016, Royal Society of Chemistry. (c) $CrGeTe_3$和$CrSiTe_3$单层中每个Cr原子的磁矩与温度的关系[61]. Copyright © 2015, American Physical Society. (d) 不同厚度$CrGeTe_3$的理论和实验居里温度[2]. Copyright © 2017, Springer Nature. (e) CrOCl和CrOBr单层的居里温度理论值[62]. Copyright © 2018, American Chemical Society. (f), (g) 单层CrSeBr的电子结构以及Γ点的能带结构[63]. Copyright © 2019, Elsevier

Figure 4 (Color online) Two-dimensional Cr based ferromagnetic semiconductor. Evolution of spin magnetic moment per unit cell (square) and magnetic susceptibility (circle) with respect to temperature of $CrSiTe_3$ (a) and $CrGeTe_3$ (b) monolayers[34]. Copyright © 2016, Royal Society of Chemistry. (c) Magnetic moment and magnetic susceptibility $CrGeTi_3$ and $CrSiTi_3$ as a function of temperatures[61]. Copyright © 2015, American Physical Society. (d) Experimental (square) and theoretical (circle) field dependence of T_C in samples of various thickness[2]. Copyright © 2017, Springer Nature. (e) Specific heat and magnization with respective to temperature for the CrOCl and CrOBr monolayers[62]. Copyright © 2018, American Chemical Society. (f) Electronic structures of CrSeBr monolayer and (g) the simplified bandstructure of CrSeBr monolayer around the Γ point [63]. Copyright © 2019, Elsevier

实验上被成功制备. 它也是一种铁磁金属, 其T_C在270~300 K之间[80]. 理论计算表明, Fe_5GeTe_2单层是铁磁金属, 有望从其块体中剥离成单层[81]. 此外, 实验上Fe_4GeTe_2和Fe_5GeTe_2块体的T_C均高于Fe_3GeTe_2的T_C(图5(e)), 有望得到更高T_C的铁磁单层[77].

2.3 铁磁半金属

由于弱的磁耦合作用, 目前理论和实验上二维

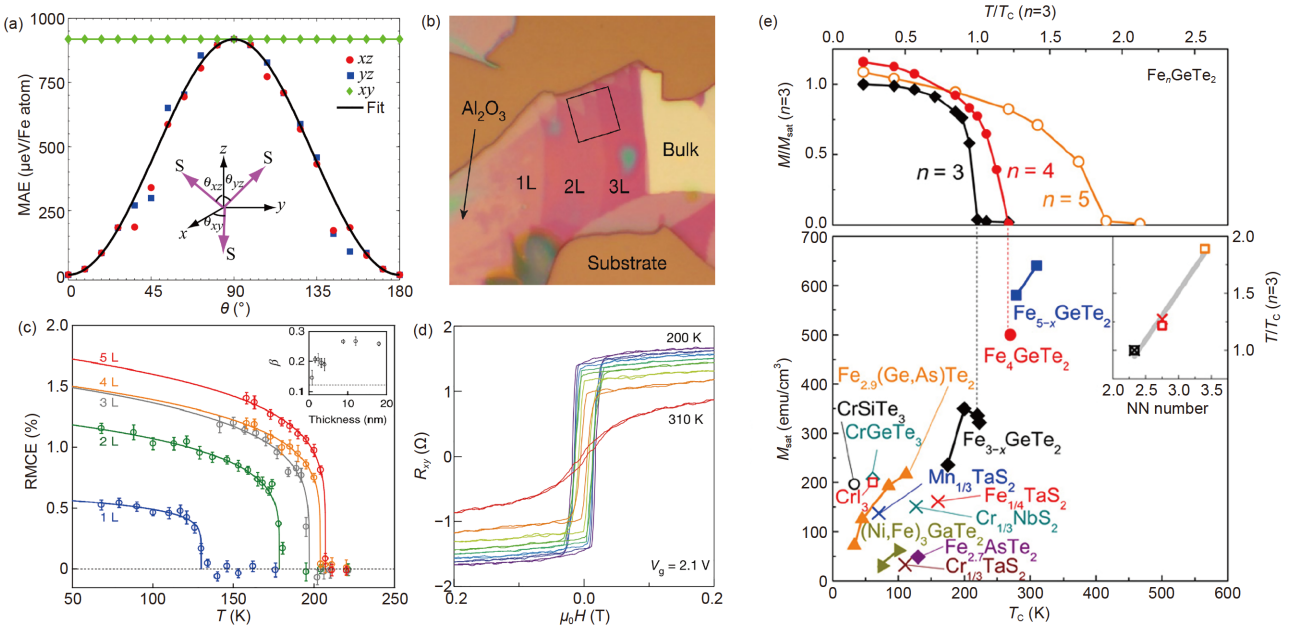

图 5 (网络版彩色)二维Fe基铁磁金属. (a) 单层Fe_3GeTe_2磁各向异性能的角度依赖关系[35]. Copyright © 2016, American Physical Society. (b) 在Al_2O_3薄膜衬底上剥离的典型少数层Fe_3GeTe_2的光学图像[19]. Copyright © 2018, Springer Nature. (c) 不同厚度的Fe_3GeTe_2居里温度测量值[18]. Copyright © 2018, Springer Nature. (d) 特定栅极电压下单层Fe_3GeTe_2表现出室温铁磁性[19]. (e) Fe_xGeTe_2(x=3, 4, 5)及其他范德华铁磁材料的磁化强度及饱和磁化强度(M_{sat})随温度的变化关系[77]. Copyright © 2019, John Wiley & Sons

Figure 5 (Color online) Two-dimensional Fe based ferromagnetic metal. (a) Angular dependence of the magnetic anisotropy energy of Fe_3GeTe_2 monolayer with the direction of magnetization lying on three different planes[35]. Copyright © 2016, American Physical Society. (b) Optical image of typical few-layer Fe_3GeTe_2 flakes exfoliated on top of an Al_2O_3 thin film[19]. Copyright © 2018, Springer Nature. (c) Criticality analysis for Fe_3GeTe_2 flakes of different thicknesses[18]. Copyright © 2018, Springer Nature. (d) Hall resistance of a four-layer Fe_3GeTe_2 flake under a gate voltage of V_g= 2.1 V[19]. (e) Magnetic properties of Fe_4GeTe_2 in comparison with other vdW ferromagnets[77]. Copyright © 2019, John Wiley & Sons

FMS的T_C都比室温低得多[3]. 尽管二维FMM通常由于较强交换作用而具有较高的T_C, 但是很难进行电场调控. 鉴于这种认知, 二维FHM成为自旋电子器件的优良载体[46,82~84]. 铁磁半金属的一个自旋通道表现为金属, 而另一通道则是半导体或绝缘体的特征(图1(c)), 理论上可以提供100%极化的自旋载流子. 截至目前, 理论上已经预测了多个二维FHM, 包括氧化物、卤化物、硅化物等. 一个典型的例子是$FeCl_2$单层(图2(f)). 块状$FeCl_2$具有范德华层状结构, 且具有反铁磁性[85]. Torun等人[86]首先通过第一性原理研究了$FeCl_2$单层的电子结构和磁学性质, 发现其具有半金属特性, 基于平均场理论计算的T_C值为17 K, 其半金属性也通过杂化交换函数得到了证实[87]. Kulish和Huang[88]基于伊辛模型的二维$FeCl_2$的T_C为109 K. Feng等人[89]使用非平衡格林函数的第一原理计算方法, 揭示了$FeCl_2$单层具有出色的自旋滤波效果、高磁阻和负微分电阻效应. 此外, 应变也可以有效地增强$FeCl_2$单层的铁磁性和磁各向异性能[90]. 最近, 两个不同的课题组分别利用分子束外延的方法在高定向热解石墨(highly oriented pyrolytic graphite, HOPG)衬底上成功制备出$FeCl_2$单层[91,92]. 此外, 杂化交换泛函的计算结果表明, 也可以将同类结构的FeI_2和$FeBr_2$单层从其范德华层状块体中剥离出来, 且它们都具有半金属特性[6,87,88].

3 结论与展望

目前, 二维铁磁材料受到广泛的关注, 有望成为下一代纳米自旋电子学的基础. 基于第一性原理计算方法, 人们已经为预测和设计低维铁磁材料付出了大量的努力, 其中的一些结果已经被实验证实, 促进了二维铁磁研究的快速发展. 本文讨论了近年在二维铁磁材料研究中一些有趣进展, 包括二维铁磁半导体/金属/半金属, 显示了第一性原理方法的强大作用. 理论模拟与实验的比较也证明了第一性原理计算的准确性和有效性. 作为重要的工具, 第一性原理计算将仍然是材料设计不可或缺的组成部分, 将为自旋电子学的发展提供强有力的推动. 尽管最近二维铁磁材料的研究取得了

巨大的成功, 但仍处于起步阶段, 寻找高T_C的二维本征铁磁体仍然是当前的重点. 未来仍面临以下几个关键挑战.

(1) 设计具有高T_C、较大面外MAE和易于实验合成的二维铁磁材料. 一方面, 通过实验验证的二维铁磁材料的类型相当有限, 需要一步丰富. 另一方面, 目前的二维铁磁材料存在T_C较低和MAE较小的缺陷, 极大地限制了其应用范围. 需要深入研究影响T_C的因素, 然后找到适当的策略来提高T_C.

(2) 提高理论预测的准确性. 由于理论本身的局限性, 需要理论和实验的紧密合作. 理论指导实验进行, 实验对理论模型进行修正和完善. 综合两者的优势, 加快二维铁磁材料的理性设计与合成. 例如, 模拟居里转变温度主要是评估环境的热扰动与体系内磁矩转动的动态强度对比, 不同的材料体系具有完全不同且复杂的内在环境状态, 因此存在不同的耦合状态. 对于此类复杂的多体问题, 参数与对应的居里温度不存在显而易见的映射函数关系, 但是居里温度和磁耦合常数J存在着正相关性. 处理该类问题, 一种方法为采用平均场理论, 忽略细节的作用, 将整体的状态描述为一个统一的平均场从而获得粗糙的结果, 但结果有时会出现严重的偏差. 另一种方式为基于马尔卡夫链的蒙特卡洛模拟方法, 通过演变的方式来模拟复杂的情况, 得到更加合理的结果. 但目前的蒙特卡洛模拟也有伊辛模型和海森堡模型. 伊辛模型假定MAE是无限大的, 一般会高估T_C, 不太符合实际情况[93]. 海森堡模型通常是更好的选择.

(3) 充分利用快速发展的二维材料数据库. 为了利用已有的材料数据库, 需要发展高通量计算方法[94~96]和机器学习算法[97~99]等高效、自动化的工具, 以避免计算成本的增加. 与常规计算模拟的方法不同, 这些方法主要依靠计算机从已有的数据中进行学习, 绕过了复杂的量子力学, 因此可以极大提高预测效率, 加速了新材料的研发进程.

(4) 设计特定功能的异质结构. 结合第一性原理方法, 需投入更多的努力去探索磁性异质结构和界面工程. 将二维磁体与非磁性材料堆叠, 如$CrGeTe_3$/In_2Se_3、WSe_2/CrI_3、VSe_2/MoS_2等[32,100,101], 不仅可以通过界面工程保护二维磁性, 还可以调控磁性性质. 可以预见在磁性异质结体系中将会出现新颖的界面耦合效应, 比如多铁性、非常规超导现象、量子反常霍尔效应、超导-铁磁异质结的拓扑效应等.

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Summary for “二维铁磁材料的理论模拟与设计”

Theoretical simulation and design of two-dimensional ferromagnetic materials

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Spintronic devices, using the spins of electrons as information processing, have generated world-wide interest. Just as graphene, transition-metal dichalcogenides, and black phosphorus revolutionized condensed matter and materials engineering, the discovery of two-dimensional (2D) van der Waals (vdW) magnetic materials is expected to open a new horizon in material science and enable the potential development of spintronics. In fact, 2D magnetism has been investigated for decades while the experimental validation was unable to achieve till recently. The recent exciting 2D ferromagnetic breakthroughs, such as monolayers CrX_3 (X = Cl, Br), monolayer Fe_3GeTe_2, and bilayer $CrGeTe_3$ from their vdW bulk down to atomically thin, have also pushed forward researches on novel magnetic properties and creative concepts. In contrast to the traditional magnetic thin films, 2D vdW ferromagnetic materials (FM) largely decouple from the substrates, allow electrical control and are open to chemical functionalization.

Without clear targets or guidelines, traditional trial-and-error experiments face the fundamental challenges of long time and high costs. Computational simulations, which serving as an important first step in exploring possible applications of new materials, can not only predict novel 2D materials but also suggest their possible synthesis routes. Many interesting cases, such as the growth of 2D borophene (B) and tellurene (Te), thermoelectricity in tin selenide (SnSe), ferroelectricity in tin telluride (SnTe), and high carrier mobilities in black phosphorene, have been confirmed by experiments, showing the accuracy of computational methods and their ability in facilitating experimental exploration in 2D space. Compared to other computational methods, the first-principles method, which has been the most widely used tools in designing new materials, only require a few basic physical constants and the atomic position coordinates. It is valuable mainly in two important aspects: (1) It can be used to predict and design new materials with novel properties, and (2) it provides understanding of the physics underlying the properties of new materials to replace the expensive and time-consuming physical test. Therefore, first-principles method based on density functional theory is effective for investigating new materials. In fact, the rapid development of 2D magnetic materials benefits from theoretical simulation. For example, the recent star ferromagnetic bilayer $CrGeTe_3$, monolayer CrI_3, and monolayer Fe_3GeTe_2 were also first predicted theoretically, and they have recently been experimentally made, which shows the strong power of first-principles calculations in designing these spintronics materials.

In this review, we highlight the overall picture of recent progress, current challenges, and future prospects on theoretical design of FM materials. We hope this review provides basic understanding the importance of first-principles calculations in facilitating new discoveries and the accurate characterization of 2D FM materials. To achieve this, we first give the reason why ferromagnetic order exists in 2D space at finite temperature theoretically. Then, we summarize the discovery processes and magnetic properties of recent landscape of several 2D ferromagnetic semiconductors, metals, and half-metals, using 2D CrI_3, $CrGeTe_3$, Fe_3GeTe_2, and $FeCl_2$ as the examples, respectively. Finally, we highlight the existing problems of designed 2D FM materials and propose possible directions in computational simulations for further development. Of course, this review cannot cover all 2D FM materials, and readers can also refer to other recent reviews and references therein for more low-dimensional FM materials.

two-dimensional materials, ferromagnetic materials, first principles, magnetic anisotropy

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