Two-dimensional ferromagnetic semiconductors of monolayer BiXO3 (X = Ru, Os) with direct band gaps, high Curie temperatures, and large magnetic anisotropy

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[拓展背景] 2D 材料、第一性原理计算、蒙特卡洛模拟、应力调控

[Ques] Two-dimensional (2D) ferromagnetic semiconductors are highly promising candidates for spintronics, but are rarely reported with direct band gaps, high Curie temperatures (Tc), and large magnetic anisotropy.

[关键问题] 如何在二维体系中实现同时具备直接带隙、高居里温度与强磁各向异性的铁磁半导体？

[Sum] Using first-principles calculations, we predict that two ferromagnetic monolayers, BiXO3 (X = Ru, Os), are such materials with a direct band gap of 2.64 and 1.69 eV, respectively. Monte Carlo simulations reveal that the monolayers show high Tc beyond 400 K. Interestingly, both BiXO3 monolayers exhibit out-of-plane magnetic anisotropy, with magnetic anisotropy energy (MAE) of 1.07 meV per Ru for BiRuO3 and 5.79 meV per Os for BiOsO3. The estimated MAE for the BiOsO3 sheet is one order of magnitude larger than that for the CrI3 monolayer (685 μeV per Cr). Based on the second-order perturbation theory, it is revealed that the large MAE of the monolayers BiRuO3 and BiOsO3 is mainly contributed by the matrix element differences between dxy and dx2–y2 and dyz and dz2 orbitals. Importantly, the ferromagnetism remains robust in 2D BiXO3 under compressive strain, while undergoing a ferromagnetic to antiferromagnetic transition under tensile strain.

[Introduction] Over the past few decades, spintronics has gained significant interest because of its potential in the development of future information technology due to its low energy consumption, highly integrated density, and rapid digital processing speeds. However, realizing spintronics in two-dimensional (2D) magnetic materials was long thought to be challenging based on the Mermin–Wagner theorem. Since recent

advancements in the experimental confirmation of 2D magnetism, particularly that observed in CrI_3 and $Cr_2Ge_2Te_6$ sheets, the investigation of 2D magnetic materials has become increasingly intensive. Despite progress, the usually weak magnetic exchange interaction renders the Curie temperature (Tc) of most experimentally realized 2D magnets at a value far below that of room temperature, which hinders their practical application. As such, discovering novel 2D magnetic systems with high Tc would be highly instructive.

As a potential avenue for spintronics, ferromagnetic semiconductors (FMSs) present an exceptional opportunity to merge conventional semiconductor electronics with non-volatile magnetic storage at finite temperatures. FMSs can be utilized for spin injection, detection, generation and manipulation by using state-of-the-art semiconductor technology. In the realm of 2D materials, the exploration of 2D FMSs is particularly intriguing as it presents an incredibly unique opportunity to uncover new physical phenomena or develop innovative electronic functionality. Early experimental realizations of 2D FMSs occurred in CrI_3 and $Cr_2Ge_2Te_6$ sheets, which prompted significant experimental and theoretical research to identify other materials. Examples include monolayer CrSX (X = Cl, Br, I), GdI_2, VI_3, VS_2, $CrWI_6$, h-CrC, $CrGa_2Se_4$, $TcSiTe_3$, and others. Most of the reported 2D FMSs are indirect band gap semiconductors; however, those with a direct band gap, especially those with room-temperature magnetism, have rarely been reported. A recent study has predicted that by introducing Mo into the CrSBr monolayer, the alloyed $CrMoS_2Br_2$ sheet satisfies these requirements. But its relatively low magnetic anisotropy energy (MAE, 123 μeV per Cr atom) could make its magnetism vulnerable to thermal fluctuations.

The aforementioned advancements in the field prompted the following question: can we discover novel 2D FMSs that have direct band gaps, high Curie temperatures, and large MAE? In this study, employing first-principles calculations, we recommend two $BiXO_3$ (X = Ru, Os) monolayers as such candidates for 2D FMSs. Phonon dispersion calculations and ab initio molecular dynamics (AIMD) simulations are conducted to confirm the stability of single layers. Our calculations indicate that $BiXO_3$ monolayers exhibit robust, long-range FM ordering with fully spin-polarized band gaps of 2.64 eV for $BiRuO_3$ and 1.69 eV for $BiOsO_3$. Using Monte Carlo simulations, we estimate the Curie temperature to be as high as 490 K for $BiRuO_3$ and 430 K for $BiOsO_3$, both above room temperature. Notably, we find that the magnetic properties of these materials can be

effectively modulated through strain engineering. The estimated MAE for the BiOsO3 sheet reaches up to 5.79 meV per Os, which is one order of magnitude larger than that of the CrI3 monolayer. This study lays the foundations for future research on these fascinating 2D intrinsic FM semiconductors.

[亮点 1] 通过第一性原理计算预测出 BiRuO3 与 BiOsO3 单层材料兼具直接带隙与室温以上的铁磁性，为高温自旋电子学器件提供潜在候选。

[亮点 2] 研究揭示其强磁各向异性主要源于 d 轨道间矩阵元差异，且磁性可通过应变实现可逆调控，展现出优异的力控磁学可调性。

[思考] ① 能否通过外电场或界面工程进一步增强 BiOsO3 的磁各向异性，从而提高其稳定性？

[思考] ② 这种具有大 MAE 的二维体系是否可与拓扑电子态或自旋轨道耦合效应结合，形成新型自旋拓扑器件？

[拓展阅读 1] 如何确定 BiXO3 的晶胞是 Cr2Ge2Te6 型而不是钙钛矿型？

[拓展阅读 1] 在确定 BiXO3 晶胞结构时，作者采用了 Cr2Ge2Te6 型而非传统钙钛矿型。原因在于二维层状化后，Bi—O—X—O 键合形成稳定的面外堆叠，而钙钛矿结构中的三维连接会破坏层间可分离性。通过比较能量最低的构型、原子层排列与对称性约束，计算表明 Cr2Ge2Te6 型更能保持二维铁磁性和结构稳定性。该晶格类型具有类似过渡金属卤化物的蜂窝平面，使得磁交换路径更短、磁有序更强，因此在二维极限下优于传统钙钛矿框架。

[拓展阅读 2] 蒙特卡洛模拟在计算中的具体作用是什么？如何实现的？相比于其他算法有什么优势？

[拓展阅读 2] 蒙特卡洛模拟在二维磁性计算中主要用于评估居里温度及热稳定性。通过将第一性原理得到的交换耦合常数输入 Heisenberg 模型，模拟原子自旋在不同温度下的涨落，从而统计出磁有序被破坏的临界温度。相较于分子动力学或均匀近似模型，蒙特卡洛算法能更真实反映多体自旋关联与随机热扰动效应，在计算高温磁性稳定性方面尤为高效。对于 BiXO3 体系，该方法验证了其在室温以上仍能保持铁磁序，是理论预测中不可或缺的环节。

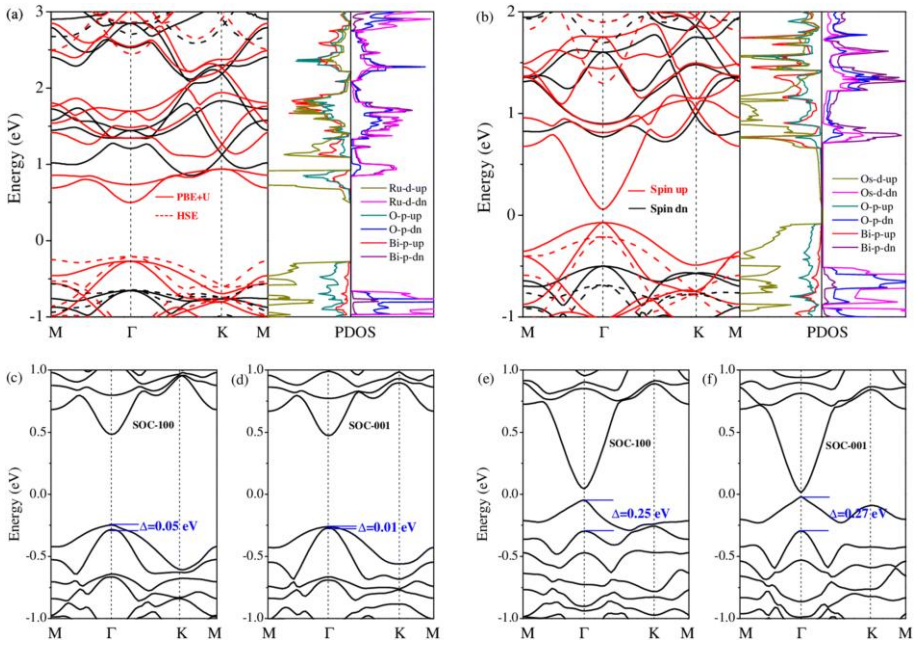
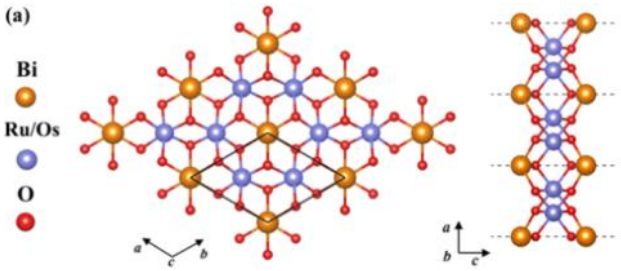


Figure 2 Spin-polarized band structures and PDOS of (a) BiRuO3 and (b) BiOsO3 monolayers using the PBE + U (solid lines) and HSE06 (dashed lines) methods. SOC band structures of (c and d) BiRuO3 and (e and f) BiOsO3 with the magnetization parallel to (100) and (001) directions. The magnetization directions and the band splitting (Δ) at the Γ point are also shown in (c–f). The Fermi level has been shifted to zero.



One-dimensional wrinkled SrRuO3 single-crystalline thin films with tunable strain gradients

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[拓展背景] 应变梯度、褶皱薄膜、柔性器件

[Ques] The flexoelectric field generated by the strain gradient possesses the capability to modify and manipulate various material characteristics. However, achieving abundant and tunable strain gradients in thin films remains a formidable challenge.

[关键问题] 如何在保持晶体完整性的同时，在氧化物薄膜中实现可调控且大幅度的应变梯度以增强挠电效应？

[Sum] In this study, we successfully transferred SrRuO3 (SRO) free-standing single-crystalline films onto a flexible PDMS substrate using a water-soluble sacrificial layer. By applying prestrain to the substrate, the transferred film exhibited a modifiable one-dimensional (1D) wrinkled structure. Through the design of a 1D wrinkled structure, a strain gradient of up to 9.6×105m−1 was introduced in the SRO film. Simultaneously, we can precisely manipulate the morphology of the wrinkles and the magnitude of the strain gradient by adjusting both the thickness of the SRO film and the level of prestrain state, thereby achieving a highly stable and flexible SRO film with a substantial strain gradient. Furthermore, we investigate the impact of strain gradient on the electrical transport properties of SRO wrinkles. It is observed that the electrical conductivity of the wrinkled films is determined by the interplay between the thickness effect and the strain gradient effect.

[Introduction] Flexoelectricity refers to the electromechanical coupling between electrical polarization and inhomogeneous deformations, such as strain gradients, in dielectric materials of any symmetry. The flexoelectric electric field generated by the strain gradient has the ability to modify and control various characteristics of materials, including defect distribution, barrier height, and photoelectric response, etc. This flexoelectric field can act independently or in combination with other built-in electric

fields. However, due to the typically small intrinsic flexoelectric coefficients, substantial flexoelectric responses require large deformations. As a result, the most pronounced manifestations of flexoelectricity are often observed at the nanoscale, where achieving large gradients is more feasible. Consequently, researchers have increasingly utilized two-dimensional nanofilms or one-dimensional nanowires to investigate flexoelectricity and its associated applications. Nevertheless, the introduction of abundant and tunable strain gradients in nanofilms or nanowires remains a challenging endeavor.

For thin films, the mainstream approach to introduce strain gradient is through the strain relaxation during epitaxial growth. For example, in the traditional planar thin film structure, the vertical strain gradient can be achieved through substrate-induced lattice mismatch, composition gradient and defect doping. Tip induction is another widely used in thin films as a simple and efficient means to apply strain gradient to samples. By using an atomic force microscope (AFM) tip or tip arrays to squeeze the surface of the sample, a very large strain gradient (106–107m−1) can be formed near the elastic deformation contact zone below the tip. Despite their high sensitivity in producing large strain gradient, these methods mentioned above do have certain limitations. Firstly, the strain gradient is highly localized, mainly concentrated at the interface, defect sites, or within a very small area beneath the tip. Secondly, the film thickness is required to be on the order of tens of nanometers to avoid irreversible damage caused by the tip. Finally, the film is clamped by a rigid substrate, which limits the transfer, integration, and flexible applications of electronic devices in many cases. In order to broaden the application of strain gradient in perovskite films, researchers have shifted their attention to flexible self-supporting films and made many attempts by using the sacrifice-layer method, such as a self-supporting membrane drum, wrinkles, etc., which provided a basis for our experiments.

In order to obtain large-area and tunable strain gradient without causing damage, we propose here to prepared one-dimensional wrinkled single-crystalline thin films with controllable structures. Since strain gradient is inversely proportional to the curvature, it can be predicted that the peaks and troughs of the wrinkled free-standing film will produce a large strain gradient due to the small curvature , which we refer to as microbending (bending on a scale of a few micrometers or even smaller). Recently, an electromechanical coupling model was developed to theoretically deal with the flexoelectricity in wrinkled thin films by Liang et al. . Large-area and tunable strain

gradients can be introduced by inhomogeneous deformation in wrinkled thin films subjected to in-plane compression. The microbending process, as described in this study, involved the transfer of a free-standing oxide thin film onto a prestrained flexible substrate. The results demonstrate that precise control over the structure of wrinkles and the size of strain gradient can be achieved by adjusting either the film thickness or the prestrain applied to the substrate. Furthermore, it has been shown that strain gradient enables tuning of the conductivity in wrinkled films.

[亮点 1] 提出可控的一维褶皱氧化物薄膜结构，通过调节预应变与厚度实现应变梯度的精准调控，最大梯度达 10^6 m^{-1}量级。

[亮点 2] 实验证实褶皱诱导的应变梯度显著影响 $SrRuO_3$的电输运性质，为利用挠电场调控氧化物电子结构提供新途径。

[思考] ① 若在褶皱 $SrRuO_3$上构建异质界面，是否能利用局域应变梯度诱导界面电荷转移或新磁序？

[思考] ② 这种可调应变梯度方法能否推广至二维材料，实现环形或二维褶皱形貌以探索拓扑挠电效应？

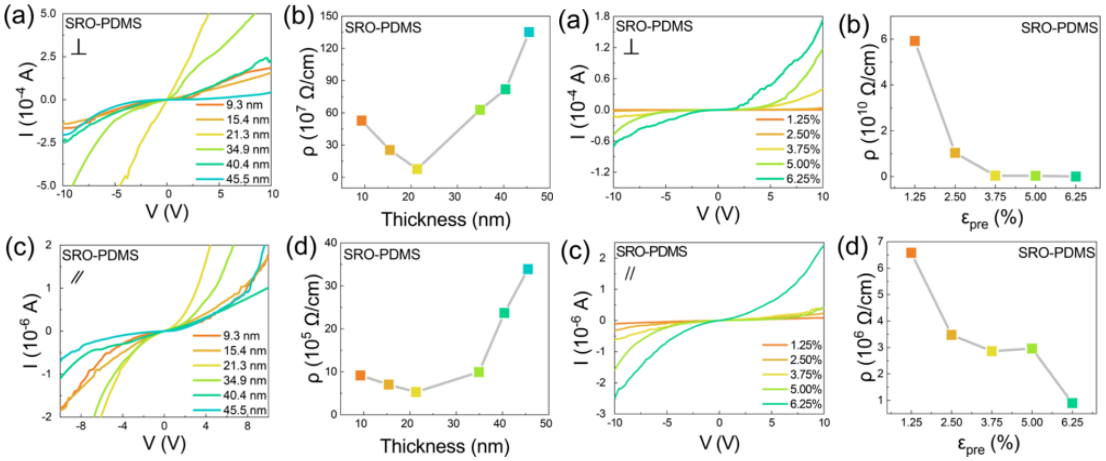
[拓展阅读 1] 挠电效应与对称性有什么关联？

[拓展阅读 1] 挠电效应（Flexoelectricity）描述的是材料在存在应变梯度时产生电极化的现象，与晶体对称性密切相关。不同于压电效应只在无中心对称晶体中存在，挠电效应在任何对称性体系中都可出现，因为应变梯度本身破坏了局域反演对称性。具体而言，当晶格某一区域被拉伸或压缩，而相邻区域保持原态时，原子位移的非对称分布会导致偶极矩的产生，从而形成挠电极化。该效应在纳米尺度尤其显著，是实现自发电势、能量收集及柔性传感器设计的重要物理基础。

[拓展阅读 2]褶皱波峰的位置是悬空的吗？褶皱延不同的晶相是否会有不同的现象？能否选择合适的预应变衬底，产生 2D 褶皱，比如环形褶皱？

[拓展阅读 2] 在一维褶皱结构中，褶皱波峰是否悬空取决于薄膜与基底的粘附能。当采用低粘附能的 PDMS 基底时，波峰区域可形成部分悬空区，产生极大的弯曲曲率与应变梯度。若沿不同晶向形成褶皱，局域电子结构和导电性也会出现明显差

异。通过选择性预应变设计，还可在二维方向上诱导环形或棋盘式褶皱，从而实现二维应变梯度场。这类结构不仅有助于探索空间调制的挠电响应，还可与铁电或自旋轨道体系耦合，形成多场响应的柔性功能器件。



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