Stabilization of a honeycomb lattice of IrO$_6$ octahedra by formation of ilmenite-type superlattices in MnTiO$_3$

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In quantum spin liquid research, thin films are an attractive arena that enables the control of magnetic interactions via epitaxial strain and two-dimensionality, which are absent in bulk crystals. Here, as a promising candidate for the development of quantum spin liquids in thin films, we propose a robust ilmenite-type oxide with a honeycomb lattice of edge-sharing IrO$_6$ octahedra artificially stabilised by superlattice formation using the ilmenite-type antiferromagnetic oxide MnTiO$_3$. Stabilised sub-unit-cell-thick Mn–Ir–O layers are isostructural to MnTiO$_3$ and have an atomic arrangement corresponding to ilmenite-type MnIrO$_3$. By performing spin Hall magnetoresistance measurements, we observe that antiferromagnetic ordering in the ilmenite Mn sublattice is suppressed by modified magnetic interactions in the MnO$_6$ planes via the IrO$_6$ planes. These findings contribute to the development of two-dimensional Kitaev candidate materials, accelerating the discovery of exotic physics and applications specific to quantum spin liquids.
Recent studies on quantum spin liquids have focused on the development of new candidate materials. In the materials design, an exactly soluble $S = 1/2$ spin model on a two-dimensional honeycomb lattice presents a rigorous theoretical framework, which was initially proposed by Kitaev and subsequently reformulated with realistic materials by Jackeli and Khaliullin. An important component of the model is a honeycomb lattice of edge-sharing metal-anion octahedra, comprising $Ru^3+$ or $Ir^4+$ ions with a $d^6$ electron configuration, which produces bond-specific Ising-like interactions, called Kitaev-type interactions, and yields strong quantum fluctuations of (pseudo) spins in the honeycomb lattice $\alpha \beta \gamma$. For $\alpha$-RuCl$_3$ and iridates such as Na$_2$IrO$_3$ (refs. 6), $\alpha$, $\beta$, and $\gamma$-Li$_2$IrO$_3$ (refs. 6–13) and H$_2$IrCl$_6$O$_3$ (ref. 14), the potential of achieving quantum spin liquids via Kitaev-type interactions has been extensively discussed. In addition to theoretical approaches, advanced experiments on bulk crystals, such as magnetic resonant X-ray diffraction (XRD) and nuclear magnetic resonance, have been used to examine complex magnetic phases and identify quantum spin liquid states.

A major challenge in this research field is to incorporate these materials in thin films, especially atomically thin monolayer forms. Thin-film techniques are essential not only for practical applications but also for providing additional degrees of freedom for the control of magnetic interactions. For example, epitaxial strain at the interface and dimensionality control can present opportunities to address the breaking of the expected Kitaev-type interactions by antiferromagnetic ordering due to structural distortion and interlayer coupling. However, high-quality films of $\alpha$-RuCl$_3$ and iridates with H and Li, which have to date attracted the attention of researchers as bulk candidate materials, are difficult to prepare. This is because their volatile and/or diffusion nature requires the precise control of stoichiometry and the suppression of inter-diffusion to reproduce the bulk properties.

Inspired by these problems in known Kitaev candidate materials, we aim to determine a new system that is suitable for thin-film research and focus on ilmenite-type $ABO_3$ compounds (where $A$ and $B$ are metal cations) containing $Ir^5$.

Recently, Haraguchi et al. proposed a method for the bulk synthesis of ilmenite-type ZnIrO$_3$ and MgIrO$_3$ with honeycomb lattices of edge-sharing IrO$_6$ octahedra in the $ab$ plane (e.g., see Fig. 1a, b). The authors discussed an $XY$-like magnetic anisotropy and a tilting magnetic structure, which may be related to Kitaev-type interactions.

This study begins with ilmenite-type MnTiO$_3$, for which the single-crystalline film growth on Al$_2$O$_3(0001)$ has been established, and attempts to stabilise Ir at the $B$-site of the ilmenite-type MnBO$_3$ (Fig. 1a, b). By adopting the epitaxial strain in superlattices with ilmenite-type MnTiO$_3$, which shares the $A$-site MnO$_6$ plane, we develop a honeycomb lattice of edge-sharing IrO$_6$ octahedra in an ilmenite lattice. This ultrathin-film form of iridate will serve as an intriguing two-dimensional platform for investigations in the physics of Kitaev materials.

**Results**

**Structural characterisation using XRD.** The films were grown on Al$_2$O$_3(0001)$ substrates (lattice constants are $a = 4.759$ Å and $c = 12.993$ Å, JCPDS PDF 00-046-1212) by pulsed-laser deposition using a KrF excimer laser (see “Methods”). Our early attempt to grow ilmenite-type MnIrO$_3$ directly on Al$_2$O$_3(0001)$ was unsuccessful and resulted in phase-separated films of MnO$_3$ and IrO$_2$ (see Supplementary Fig. 1 in Supplementary Information for the XRD pattern). We then employed a superlattice approach based on ilmenite-type MnTiO$_3$ thin films. In the superlattice structure, the common $A$-site MnO$_6$ plane is expected to promote the ilmenite-type stacking of MnO$_6$ and IrO$_6$ planes along the $c$-axis direction (Fig. 1a, b). The schematic structure of a typical superlattice is shown in Fig. 1c, where a MnTiO$_3$ buffer layer with a thickness ranging between 4.3 and 7.8 nm was initially grown on Al$_2$O$_3(0001)$, followed by the alternate deposition of much thinner Mn–Ir–O and MnTiO$_3$ layers. A film thickness of 1.4 nm is approximately equal to the order of magnitude of typical $c$-axis parameters of ilmenite-type oxides. In a 0.5-nm-thick Mn–Ir–O (cap)/4.3-nm-thick MnTiO$_3$/0.5-nm-thick Mn–Ir–O$_{1.5}$/5.7-nm-thick MnTiO$_3$ (buffer) film (superlattice cycle number $n = 15$ in Fig. 1c), the overall chemical composition of the film evaluated using energy-dispersive X-ray spectroscopy (EDX) was MnTiIr = 50:45:4:5:5, which is in good agreement with the ideal composition of MnTiIr = 50:44:9:5:1, as expected from the design thickness ratio. In the out-of-plane XRD pattern shown in Fig. 1d, four main diffraction peaks are observed from the film and are assigned to (0003m) ($m$: natural number) of the ilmenite-type structure. The satellite peaks near the (0006) and (00012) peaks (denoted by red arrows) indicate periodic modulation in the X-ray scattering cross-section by the superstructure of MnTiO$_3$ and Mn–Ir–O layers, verifying that no alloy compound of MnTiIr$_{0.5}$O$_{1.5}$ was formed. Assuming an abrupt MnTiO$_3$/Mn–Ir–O interface without inter-diffusion, the average in- and out-of-plane lattice parameters of the single unit of the superlattice, that is, $[4.3$-nm-thick MnTiO$_3$]/0.5-nm-thick Mn–Ir–O$_{1.5}$, were $a = 5.139$ Å and $c = 14.29$ Å from the reciprocal space mapping near (02210) (Fig. 1e).

Because these values differ insignificantly from $a = 5.1396$ Å and $c = 14.29$ Å of MnTiO$_3$ (JCPDS PDF No. 00-029-0902), the lattice parameters of Mn–Ir–O are comparable with those of MnTiO$_3$. In addition, the threefold symmetry of the (1014) diffraction peak was detected in the in-plane azimuthal $\phi$ scan measurements (Fig. 1f, g), indicating the epitaxial orientation relationship of the film [1010]//(0001)//Al$_2$O$_3$ [1010](0001). These results indicate that the film grows as a $c$-axis-oriented, single-domain, ilmenite-type oxide with a periodically modulated internal structure.

We examined the critical $d_{\text{MIO}}$ value to maintain the single-domain film growth by varying the thickness of the Mn–Ir–O layers ($d_{\text{MIO}}$) in the [4.3-nm-thick MnTiO$_3$/$d_{\text{MIO}}$-nm-thick Mn–Ir–O$_{1.5}$ superlattice. As shown in Fig. 2a, b, the films with $d_{\text{MIO}} = 0.5$ nm (identical to the sample in Fig. 1) and 1.0 nm exhibit clear (0006) peaks, which are associated with satellite peaks (red arrows). In particular, for $d_{\text{MIO}} = 0.5$ nm, thickness fringes appear near the (0006) peak, indicating that the total film thickness is uniform over the entire film. Considering the observed satellite peaks as superlattice reflections, the single-unit lengths of the superlattices were calculated to be 4.5 nm and 5.6 nm for $d_{\text{MIO}} = 0.5$ nm and $d_{\text{MIO}} = 1.0$ nm, respectively. This is consistent with the designed values of 4.8 nm ($=4.3+0.5$ nm) and 5.3 nm ($=4.3+1.0$ nm), respectively. However, in the thickest film with $d_{\text{MIO}} = 1.4$ nm (Fig. 2c), superlattice reflections become indiscernible with the occurrence of a diffraction peak of segregated IrO$_2$ impurities; the designed superlattice structure is no longer formed for $d_{\text{MIO}} = 1.4$ nm. The decrease in the (0006) diffraction intensity implies that the basal MnTiO$_3$ layers in the superlattice are disordered. Therefore, the upper bound of $d_{\text{MIO}}$ for stabilising the IrO$_2$ planes in the ilmenite lattice is ~1.0 nm, which is smaller than typical $c$-axis parameters of ilmenite-type oxides (~1.4 nm). The sub-unit-cell-thick Mn–Ir–O layer admits at most two IrO$_2$ planes, indicating the fragile crystalline phase of Mn–Ir–O. Sandwiching between stable MnTiO$_3$ layers in the superlattice structure stabilises the ilmenite-type atomic ordering of Mn–Ir–O ultrathin layers.

**Microstructural characterisation by scanning transmission electron microscopy (STEM).** The suitability of our method for the formation of honeycomb-lattice IrO$_6$ planes was verified by
IrO₆ and MnO₆ planes corresponds to the 2/3-unit cell (u.c.) of VESTA (ref. 51).

(4 u.c.). Red arrows and asterisks indicate superlattice re

Schematic structure of a Mn

angle annular dark-

parallel to the

see Supplementary Fig. 2 for the XRD pattern), eight bright layers

ordering. Note that the Mn

plane X-ray diffraction (XRD) pattern of a

around Al₂O₃

Owing to the

characteristic atomic arrangement. From these results, we con-

ment in the image, we determined that Ir atoms are located at the

large lattice mismatch of ~8% between MnTiO₃ and Al₂O₃ and

bright island-like regions are observed, which may be due to the

reduction, the presence of an oxygen deficiency is expected from the O K-edge spectra. We inferred that Mn²⁺ and Ir⁴⁺ are stable under the oxygen pressure of 10 mTorr used for the deposition, whereas Ti⁴⁺ is reduced to Ti³⁺. Charge transfer between B-site TiO₆ and IrO₆ planes via A-site MnO₆ planes may be related to this point, although it is currently unclear.

Investigation of surface magnetic order using spin Hall magnetoresistance measurements. Based on these structural analyses, a honeycomb lattice of edge-sharing IrO₆ octahedra partly forms a two-dimensional network in a superlattice. In Ir⁴⁺-containing oxides, the delicate interplay of moderate electronic correlations and spin–orbit coupling determines whether the electronic structure of a material is metallic (gapless)27–32 or insulating (gapped)1,33,34. Our superlattice samples were highly insulating (not shown), indicating the non-metallic electronic structure of Mn—Ir—O. Magnetism in ultrathin films, particularly for cases of antiferromagnetism and quantum spin liquids, is difficult to evaluate using bulk experimental methods10,13–15. Thus, we studied the surface magnetic order using the spin Hall magnetoresistance (SMR) method, which enables electrical characterisation of ferromagnetic35 and antiferromagnetic transitions36–38, as well as magnetic anisotropy. By measuring the SMR at the interface of Pt and MnTiO₃ ultrathin films, we recently demonstrated that bulk Néel temperature \( T_N \) (~63 K)39 and uniaxial magnetic anisotropy along the c-axis direction persist down to a film thickness of 2.9 nm ~2 u.c. with six
MnO₆ planes. For the present experiment, we examined five different heterostructures, as shown in Fig. 4a: Pt/4.3-nm-thick MnTiO₃ (~3 u.c., thick MnTiO₃), Pt/1.0-nm-thick Mn–Ir–O/4.3-­
nm-thick MnTiO₃ (bilayer) and Pt/1.0-nm-, 1.9-nm- and 4.3-nm-thick MnTiO₃/1.0-nm-thick Mn–Ir–O/4.3-nm-thick MnTiO₃ samples (trilayers A, B and C, respectively) (see Supplementary Fig. 5 for their XRD patterns). As shown in the inset of Fig. 4b (“Methods”), we simultaneously measured the resistances of the two orthogonal Pt channels (i.e., \( R_1 \) for channel 1, and \( R_2 \) for channel 2) under an in-plane magnetic field \( H \) applied parallel to channel 1. Figure 4b–d show the temperature \( T \) dependence of the field-induced resistance variation, \( \Delta R = (R_1/R_2)_0.5 T - (R_1/R_2)_0 T \). Here, \( (R_1/R_2)_0.5 T \) and \( (R_1/R_2)_0 T \) are the resistance ratios measured at \( \mu_0 H = 0.5 T \) and 0 T (where \( \mu_0 \) is the vacuum permeability), respectively. If an antiferromagnetic transition occurs in the layer beneath the Pt layer, distinct SMR responses of \( R_1 \) and \( R_2 \) below and above \( T_N \) result in an inflection in \( \Delta R \) (refs. 22,36,37). In fact, the value of \( \Delta R \) for both the thick-MnTiO₃ monolayer (Fig. 4b) and trilayer C (purple in Fig. 4d) exhibits a sudden increase near \( T = 60 \) K upon heating, wherein bulk MnTiO₃ undergoes an antiferromagnetic-to-paramagnetic transition36. These results indicate that an antiferromagnetic order develops in the 4.3-nm-thick MnTiO₃ top layers (~3 u.c. with nine MnO₆ planes) regardless of the underlying Al₂O₃(0001) substrate or the 1.0-nm-thick Mn–Ir–O/4.3-nm-thick MnTiO₃/Al₂O₃(0001) structure. In stark contrast, the \( \Delta R \) value for the bilayer (Fig. 4c) and trilayers A and B (green and light blue in Fig. 4d) exhibits a gradual increase with increasing \( T \) without definite anomalies. Although A-site spinful MnO₆ planes are common to all samples, their magnetic ordering behaviours are completely different. This may indicate the magnetic interactions in Mn–Ir–O, that is, the unique stacking of the honeycomb-lattice IrO₆ and MnO₆ planes.

Discussion
Comparing the SMR results, we discuss the possible magnetic properties of Mn–Ir–O. In the thick-MnTiO₃ monolayer and trilayer C terminated with 3-u.c.-thick MnTiO₃ top layers, nine MnO₆ layers are positioned beneath the Pt layer. The \( T_N \) (the inflection in \( \Delta R \)) detected in the thick samples is consistent with the robust antiferromagnetic ordering in MnTiO₃ monolayers previously reported22. The absence of such signatures in the Mn–Ir–O cap layer viewed along the Al₂O₃ [1120] direction. **a** Wide area; scale bar: 10 nm. **b** MnTiO₃/Mn–Ir–O/MnTiO₃ interface region; scale bar: 2 nm. **c** Atomically resolved images; scale bar: 1 nm (the area marked by yellow dashed lines in **b**). **d** Schematic crystal structure corresponding to **c**. HAADF high-angle annular dark-field, STEM scanning transmission electron microscopy.
bilayer indicates locally modified super-exchange interactions in the MnO₆ planes by intervening in the IrO₆ planes. Considering the strong spin–orbit coupling, which is inherent to heavy Ir (refs. 1,27–34), a disruption of the antiferromagnetic order may occur. Figure 4e, f schematically show a possible picture of spin interactions between the Mn sites (black arrows) in the bilayer, where the antiferromagnetic order develops in the MnTiO₃ bottom layer, except the overgrown Mn–Ir–O layer. In the thin-MnTiO₃ top layers (~2 u.c.) of trilayers A and B, a similar spin fluctuation may be caused by the neighbouring IrO₆ planes.

Extrinsic contributions, such as the surface roughness and the effect of size (refs. 40–42), should also be considered to understand the suppression of antiferromagnetic order in thin-MnTiO₃ (~2 u.c.) and Mn–Ir–O top layers. Firstly, all measured samples had smooth surfaces with root-mean-square roughness values ranging from 0.2 to 1.0 nm, which cannot exclusively account for the distinct SMR responses. Furthermore, despite its island-like film morphology with increased surface roughness, the 2-u.c.-thick thin-MnTiO₃ monolayer exhibits a bulk-like $T_N$ as in thicker and flatter samples (~3 u.c.)22, supporting the negligible role of the surface roughness. Secondly, the total film thicknesses of the heterostructures (including MnTiO₃ and Mn–Ir–O layers) are significantly thicker than the 2 u.c.; therefore, a sufficiently large volume of the Mn sublattice is guaranteed for the entire heterostructure. This also helps minimise the potential influence of domain disconnection, which is generally pronounced in ultrathin films. In stark contrast, there is a systematic recovery of antiferromagnetic SMR responses with an increase in the

Fig. 4 Spin Hall magnetoresistance measurements. a Schematic structures for the 4.3-nm-thick MnTiO₃ monolayer (thick MnTiO₃), 1.0-nm-thick Mn–Ir–O/4.3-nm-thick MnTiO₃ bilayer (bilayer) and 1.0-nm-, 1.9-nm- and 4.3-nm-thick MnTiO₃/1.0-nm-thick Mn–Ir–O/4.3-nm-thick MnTiO₃ trilayer (trilayer A, B and C, respectively) samples. A thickness of 1.4 nm corresponds to ~1 u.c. height of their ilmenite lattices along the out-of-plane c-axis direction. b–d Field-induced variation ($\mu_0H = 0.5$ T) in the resistance ratio of two orthogonal Pt channels, $R_1/R_2$, for b, the thick MnTiO₃, c the bilayer and d trilayers A, B and C. In the thick-MnTiO₃ monolayer (Fig. 4b) and trilayer C (Fig. 4d), SMR responses indicating antiferromagnetic transition were detected. The inset in b shows the measurement setup, where $R_1$ and $R_2$ are measured simultaneously under an in-plane magnetic field $H$ applied parallel to channel 1 with $R_1$ (perpendicular to channel 2 with $R_2$). $E_1$ and $E_2$ are the electrodes used for current injection. e, f Schematic for the spin ordering at Mn sites in the Mn–Ir–O/MnTiO₃ bilayer sample expected from the SMR responses. e Metal-oxygen octahedra in the ab plane. Small red spheres represent O ions. Yellow-coloured octahedra are located above the grey coloured octahedra. f Cross-sectional view along the $[11\overline{2}0]$ direction. The pink, light blue and brown spheres represent Ir, Mn and Ti ions, respectively, and are positioned in the oxygen octahedra. Only the localised moments of Mn ions are depicted by black arrows.
thickness of the MnTiO3 top layer from trilayer A (2/3 u.c.), B (4/3 u.c.) and C (3 u.c.), which indicates the intrinsic origin that is responsible for spin interactions in a characteristic length. Notably, the clear difference observed between the antiferromagnetic 2-u.c.-thick thin-MnTiO3 monolayer22 and the non-antiferromagnetic trilayer B (4/3-u.c.-thick MnTiO3 and 2/3-u.c.-thick Mn—Ir—O (2 u.c. in total) on the MnTiO3 buffer) indicates that the insertion of honeycomb-lattice IrO6 planes affects the spin interactions between nearby Mn sites. Such a spin-disordered (or spin-frustrated) state may be associated with quantum spin liquids, although the experimental identification of the featureless magnetic ground state in ultrathin films presents a great challenge43−45. The next step is to understand the spin structures (including the Ir sites) and the excited-state properties in Mn—Ir—O using recently advanced diagnostics such as Raman spectroscopy15,46 and in-plane spin transport measurements47−50. In addition, the structural quality of a sample is important for the formation of pure Kitaev materials. In particular, the interface roughness (Fig. 3b), oxygen vacancies (Supplementary Fig. 4) and possible inter-diffusion can be the source of local structural distortions that destroy Kitaev-type interactions via the non-ideal splitting of Ir 5d orbitals.20 Nevertheless, the suppression of the strong antiferromagnetic order in the Mn sublattice is promising for demonstrating the feasibility of controlling spin interactions by artificially engineered ilmenite-type oxides.

In summary, we have materialised a honeycomb lattice of edge-sharing IrO6 octahedra by using a superlattice formation with ilmenite-type MnTiO3. Systematic SMR measurements indicated the absence of antiferromagnetic order in the surface Mn—Ir—O layer grown on antiferromagnetic MnTiO3. Although A-site MnO6 planes are common to these oxides, the spin interactions between the Mn sites are different. Spin fluctuations induced by strong spin–orbit interactions in the IrO6 planes can disrupt the antiferromagnetic ordering in the Mn—Ir—O layer and the neighbouring regions of the MnTiO3 layers. The stabilisation of a two-dimensional IrO6 honeycomb lattice using the superlattice technique, as well as the potential control of the magnetism via dimensionality and the proximity effect, is expected to trigger the development of ilmenite-based Kitaev materials that produce exotic physical phenomena.

Methods

Thin-film growth. The Mn—Ir—O target was prepared from MnO2 and IrO2 powders by spark-plasma-sintering at 50 MPa and 900 °C. The target composition, as measured by EDX, was MnIr 60:1 (atomic ratio). The MnTiO3 buffer layer was grown at a substrate temperature of 850 °C and an oxygen pressure of 10 mTorr using the Mn—Ti—O target22. Subsequently, Mn—Ir—O and MnTiO3 layers were alternately deposited for n cycles at 800 °C and 10 mTorr for the formation of a [Mn—Ir—O/MnTiO3]n superlattice. The crystal structure and composition of the films were characterised by XRD using Cu Kα radiation and EDX, respectively.

SMR measurements. A Pt film with a thickness of ~2 nm was deposited on the film surface by radio-frequency magnetron sputtering at 150 °C. The heterostructure film was then patterned into an L-shaped multiterminal device structure using photolithography and Ar ion milling, followed by the electron-beam evaporation of Au/Ti electrodes. The resistance was measured by the four-probe method using a semiconductor parameter analyser (Agilent 4155C) and a nano-volt metre (Keithley 2182A) in a physical property measurement system (Quantum Design, Inc.) equipped with a one-axis sample rotator. The direction (polarity) of the current I was varied during the measurements, and the averaged resistance values, \( R_{\pm} = \frac{R_{+} \pm R_{-}}{2} \) (\( j = 1 \) and 2), were used for the analysis. Details of the measurement scheme and analysis are reported in ref.22.

Electron microscopy. To obtain an electron-transparent thin specimen, the thin film with the substrate was mechanically polished, and Ar ion beam milling was performed at 0.5 kV in the final stage. For the atomic and electronic structure analyses, an aberration-corrected STEM system (JEOL ARM300CF equipped with a DELTAFast detector, cold-field emission gun and EELS spectrometer (Quantum, Gatan, Inc.) operated at 300 kV was used. The probe-forming aperture was 30 mrad, and the collection semi-angle for HAADF was 85–200 mrad.

Data availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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Author contributions

K.M. grew the films and performed the SMR measurements along with K.F. K.N., R.I. and N.S. conducted the STEM analysis. K.F., K.M. and A.T. wrote the paper with input from the other authors. All authors discussed the results. A.T. supervised the project.

Competing interests

The authors declare no competing interests.

Additional information

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