ARTICLE

<https://doi.org/10.1038/s43246-020-00059-1>

OPEN

Stabilization of a honeycomb lattice of IrO_6 octahedra by formation of ilmenite-type superlattices in MnTiO_3

Kei Miura¹, Kohei Fujiwara¹✉, Kei Nakayama², Ryo Ishikawa^{2,3}, Naoya Shibata² & Atsushi Tsukazaki^{1,4}

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.

¹Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan. ²Institute of Engineering Innovation, The University of Tokyo, Tokyo 113-8656, Japan. ³PRESTO, Japan Science and Technology Agency, Kawaguchi 332-0012, Japan. ⁴Center for Spintronics Research Network (CSRN), Tohoku University, Sendai 980-8577, Japan. ✉email: kfujiwara@imr.tohoku.ac.jp

Recent studies on quantum spin liquids have focused on the development of new candidate materials¹. In the materials design, an exactly solvable $S = 1/2$ spin model on a two-dimensional honeycomb lattice presents a rigorous theoretical framework, which was initially proposed by Kitaev² and subsequently reformulated with realistic materials by Jackeli and Khaliullin³. 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^5 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^{4,3–5}. For $\alpha\text{-RuCl}_3$ (refs. 6,7) and iridates such as Na_2IrO_3 (refs. 8,9), α -, β - and γ - Li_2IrO_3 (refs. 9–13) and $\text{H}_3\text{LiIr}_2\text{O}_6$ (ref. 14), the potential of achieving quantum spin liquids via Kitaev-type interactions has been extensively discussed. In addition to theoretical approaches^{3–5}, advanced experiments on bulk crystals, such as magnetic resonant X-ray diffraction (XRD)^{10,13}, the thermal Hall effect¹⁵ and nuclear magnetic resonance¹⁴, 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^{16–18} can present opportunities to address the breaking of the expected Kitaev-type interactions by antiferromagnetic ordering due to structural distortion and inter-layer coupling^{6–13,19,20}. However, high-quality films of $\alpha\text{-RuCl}_3$ (refs. 6,7) and iridates with H and Li (refs. 10–14), which have to date attracted the attention of researchers as bulk candidate materials, are difficult to prepare. This is because their volatile and/or diffusible 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 crystal 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^{19,20}. 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 plane¹⁹ (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 interactions¹⁹.

This study begins with ilmenite-type MnTiO_3 , for which the single-crystalline film growth on $\text{Al}_2\text{O}_3(0001)$ has been established^{21,22}, 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 $\text{Al}_2\text{O}_3(0001)$ substrates (lattice constants are $a = 4.759 \text{ \AA}$ and $c = 12.993 \text{ \AA}$, 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 $\text{Al}_2\text{O}_3(0001)$ was unsuccessful and resulted in phase-separated films of Mn_3O_4 and IrO_2 (see Supplementary Fig. 1 in Supplementary Information for the XRD pattern). We then employed a superlattice approach^{16–18} based on ilmenite-type MnTiO_3 thin films^{21,22}. 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 $\text{Al}_2\text{O}_3(0001)$, 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]₁₅/5.7-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 Mn:Ti:Ir = 50.4:45.1:4.5, which is in good agreement with the ideal composition of Mn:Ti:Ir = 50.0:44.9:5.1, 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 (0003 m) (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 Mn(Ti,Ir) O_3 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], were $a = 5.13 \text{ \AA}$ and $c = 14.29 \text{ \AA}$ from the reciprocal space mapping near (02210) (Fig. 1e). Because these values differ insignificantly from $a = 5.1396 \text{ \AA}$ and $c = 14.29 \text{ \AA}$ 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 ϕ scan measurements (Fig. 1f, g), indicating the epitaxial orientation relationship of the film [1010](0001)// Al_2O_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_{MIO} value to maintain the single-domain film growth by varying the thickness of the Mn–Ir–O layers (d_{MIO}) in the [4.3-nm-thick MnTiO_3 / d_{MIO} -nm-thick Mn–Ir–O]₁₅ superlattice. As shown in Fig. 2a, b, the films with $d_{\text{MIO}} = 0.5 \text{ nm}$ (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 $d_{\text{MIO}} = 0.5 \text{ nm}$, 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 $d_{\text{MIO}} = 0.5 \text{ nm}$ and $d_{\text{MIO}} = 1.0 \text{ nm}$, respectively. This is consistent with the designed values of 4.8 nm ($= 4.3 + 0.5 \text{ nm}$) and 5.3 nm ($= 4.3 + 1.0 \text{ nm}$), respectively. However, in the thickest film with $d_{\text{MIO}} = 1.4 \text{ nm}$ (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 $d_{\text{MIO}} = 1.4 \text{ nm}$. 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_{MIO} for stabilising the IrO_6 planes in the ilmenite lattice is $\sim 1.0 \text{ nm}$, which is smaller than typical c -axis parameters of ilmenite-type oxides ($\sim 1.4 \text{ nm}$). The sub-unit-cell-thick Mn–Ir–O layer admits at most two IrO_6 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

Fig. 1 Superlattices of ilmenite-type MnTiO_3 and Mn–Ir–O . **a** Crystal structure of ilmenite-type MnBO_3 viewed along the $[11\bar{2}0]$ direction, drawn by VESTA (ref. 51). **b** Honeycomb lattice formed by edge-sharing BO_6 octahedra in the ab plane. The black quadrangles in **a** and **b** represent the unit cell. **c** Schematic structure of a $\text{Mn–Ir–O}(\text{cap})/[\text{d}_{\text{MTO}}\text{-nm-thick MnTiO}_3/\text{d}_{\text{MIO}}\text{-nm-thick Mn–Ir–O}]_n/\text{MnTiO}_3(\text{buffer})$ film grown on $\text{Al}_2\text{O}_3(0001)$. **d** Out-of-plane X-ray diffraction (XRD) pattern of a film with $d_{\text{MTO}} = 4.3$ nm (3 u.c.), $d_{\text{MIO}} = 0.5$ nm and $n = 15$. The thickness of the MnTiO_3 buffer layer was 5.7 nm (4 u.c.). Red arrows and asterisks indicate superlattice reflections and forbidden $\text{Al}_2\text{O}_3(0003m)$ reflections, respectively. **e** Reciprocal space mapping around $\text{Al}_2\text{O}_3(02\bar{2}10)$. **f, g** In-plane ϕ scan results for $(10\bar{1}4)$ peaks of Al_2O_3 substrate and film, respectively.

cross-sectional STEM observations (see “Methods”). In a $[\text{MnTiO}_3/\text{Mn–Ir–O}]_8/\text{MnTiO}_3(\text{buffer})$ film (no Mn–Ir–O cap; see Supplementary Fig. 2 for the XRD pattern), eight bright layers parallel to the film plane were detected in the wide-area high-angle annular dark-field (HAADF) image, as shown in Fig. 3a. Owing to the Z-contrast nature (Z: atomic number)²³, the bright layers should contain a significant amount of Ir, which has the largest Z among the constituent elements (Mn, Ti, Ir and O). Tiny bright island-like regions are observed, which may be due to the presence of segregated Ir-rich impurities. As expected from the large lattice mismatch of $\sim 8\%$ between MnTiO_3 and Al_2O_3 and the observed relaxed growth (e.g., Fig. 1e), geometrical misfit dislocations were formed around the MnTiO_3 buffer/ Al_2O_3 substrate interface (Supplementary Fig. 3). A thorough inspection of a single unit of the superlattice (Fig. 3b) revealed that a Mn–Ir–O layer between MnTiO_3 layers contains some bright atomic planes along the $[0001]$ direction. Using the atomically resolved HAADF image in Fig. 3c (the area marked by yellow dashed lines in Fig. 3b), we compared each atomic site with a model structure (Fig. 3d). For MnTiO_3 , the MnO_6 (TiO_6) plane had a larger (smaller) atomic displacement along the $[0001]$ direction between the in-plane Mn (Ti) ions²⁴. By measuring the atomic displacement in the image, we determined that Ir atoms are located at the B-site, which is occupied by Ti atoms in MnTiO_3 , as schematically shown in Fig. 3d (also see in the left side of Fig. 3c). In addition, the bright Ir-containing planes are regularly sandwiched between the MnO_6 planes and have a similar dumbbell-like characteristic atomic arrangement. From these results, we concluded that a honeycomb lattice of edge-sharing IrO_6 octahedra crystallises in the Mn–Ir–O layer with ilmenite-type atomic ordering. Note that the Mn–Ir–O layer comprising two pairs of IrO_6 and MnO_6 planes corresponds to the $2/3$ -unit cell (u.c.) of

the ilmenite lattice (Fig. 1a). We also performed electron energy loss spectroscopy (EELS) for the Mn L, Ti L and O K edges in the MnTiO_3 buffer and Mn–Ir–O layer regions (Supplementary Fig. 4). Although the Mn L-edge spectra of the two regions (i.e., Mn^{2+}) are in good agreement, a partial reduction of Ti^{4+} to Ti^{3+} occurred near the Mn–Ir–O layer^{25,26}. Associated with this reduction, the presence of an oxygen deficiency is expected from the O K-edge spectra. We inferred that Mn^{2+} and Ir^{4+} are stable under the oxygen pressure of 10 mTorr used for the deposition, whereas Ti^{4+} is reduced to Ti^{3+} . Charge transfer between B-site TiO_6 and IrO_6 planes via A-site MnO_6 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 IrO_6 octahedra partly forms a two-dimensional network in a superlattice. In Ir^{4+} -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 methods^{10,13–15}. Thus, we studied the surface magnetic order using the spin Hall magnetoresistance (SMR) method, which enables electrical characterisation of ferromagnetic³⁵ and antiferromagnetic transitions^{36–38}, as well as magnetic anisotropy. By measuring the SMR at the interface of Pt and MnTiO_3 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 planes²². 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-

Fig. 2 Examination of critical d_{MIO} values. a–c Out-of-plane X-ray diffraction (XRD) patterns for d_{MIO} -nm-thick Mn–Ir–O(cap)/[4.3-nm-thick MnTiO₃/ d_{MIO} -nm-thick Mn–Ir–O]₁₅/5.7-nm-thick MnTiO₃(buffer) films with d_{MIO} values of 0.5 nm, 1.0 nm and 1.4 nm, respectively.

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, $\Delta R = (R_1/R_2)_{0.5 \text{ T}} - (R_1/R_2)_{0 \text{ T}}$. Here, $(R_1/R_2)_{0.5 \text{ T}}$ and $(R_1/R_2)_{0 \text{ T}}$ are the resistance ratios measured at $\mu_0 H = 0.5 \text{ T}$ and 0 T (where μ_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 ΔR (refs. 22,36,37). In fact, the value of ΔR for both the thick-MnTiO₃ monolayer (Fig. 4b) and trilayer C (purple in Fig. 4d) exhibits a sudden increase near $T = 60 \text{ K}$ 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 ΔR 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 ΔR) detected in the thick samples is consistent with the robust antiferromagnetic ordering in MnTiO₃ monolayers previously reported²². The absence of such signatures in the

Fig. 3 Scanning transmission electron microscopy. HAADF-STEM images of a [MnTiO₃/Mn–Ir–O]₈/MnTiO₃(buffer) film (without a Mn–Ir–O cap layer) viewed along the Al₂O₃[11 $\bar{2}$ 0] 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.

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 ($\mu_0 H = 0.5$ 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 $[11\bar{2}0]$ 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.

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 ($\ll 2$ 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 ($\ll 2$ 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

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 anti-ferromagnetic 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 challenge^{43–45}. 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 spectroscopy^{1,5,46} and in-plane spin transport measurements^{47–50}. 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 orbitals²⁰. 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 Mn:Ir = 0.90:1 (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 K_α 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 nanovolt 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, $R_j = \frac{R_j(+I) + R_j(-I)}{2}$ (*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 DELTA corrector, 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.

Received: 9 May 2020; Accepted: 13 July 2020;

Published online: 12 August 2020

References

1. Takagi, H., Takayama, T., Jackeli, G., Khaliullin, G. & Nagler, S. E. Concept and realization of Kitaev quantum spin liquids. *Nat. Phys. Rev.* **1**, 264–280 (2019).
2. Kitaev, A. Anyons in an exactly solved model and beyond. *Ann. Phys.* **321**, 2–111 (2006).
3. Jackeli, G. & Khaliullin, G. Mott insulators in the strong spin-orbit coupling limit: from Heisenberg to a quantum compass and Kitaev models. *Phys. Rev. Lett.* **102**, 017205 (2009).
4. Savary, L. & Balents, L. Quantum spin liquids: a review. *Rep. Prog. Phys.* **80**, 016502 (2017).
5. Motome, Y. & Nasu, J. Hunting Majorana fermions in Kitaev magnets. *J. Phys. Soc. Jpn.* **89**, 012002 (2020).
6. Sears, J. A. et al. Magnetic order in α -RuCl₃: a honeycomb-lattice quantum magnet with strong spin-orbit coupling. *Phys. Rev. B* **91**, 144420 (2015).
7. Cao, H. B. et al. Low-temperature crystal and magnetic structure of α -RuCl₃. *Phys. Rev. B* **93**, 134423 (2016).
8. Singh, Y. & Gegenwart, P. Antiferromagnetic Mott insulating state in single crystals of the honeycomb lattice material Na₂IrO₃. *Phys. Rev. B* **82**, 064412 (2010).
9. Singh, Y. et al. Relevance of the Heisenberg-Kitaev model for the honeycomb lattice iridates A₂IrO₃. *Phys. Rev. Lett.* **108**, 127203 (2012).
10. Biffin, A. et al. Unconventional magnetic order on the hyperhoneycomb Kitaev lattice in β -Li₂IrO₃: full solution via magnetic resonant x-ray diffraction. *Phys. Rev. B* **90**, 205116 (2014).
11. Takayama, T. et al. Hyperhoneycomb iridate β -Li₂IrO₃ as a platform for Kitaev magnetism. *Phys. Rev. Lett.* **114**, 077202 (2015).
12. Modic, K. A. et al. Realization of a three-dimensional spin–anisotropic harmonic honeycomb iridate. *Nat. Commun.* **5**, 4203 (2014).
13. Biffin, A. et al. Noncoplanar and counterrotating incommensurate magnetic order stabilized by Kitaev interactions in γ -Li₂IrO₃. *Phys. Rev. Lett.* **113**, 197201 (2014).
14. Kitagawa, K. et al. A spin–orbital-entangled quantum liquid on a honeycomb lattice. *Nature* **554**, 341–345 (2018).
15. Kasahara, Y. et al. Majorana quantization and half-integer thermal quantum Hall effect in a Kitaev spin liquid. *Nature* **559**, 227–231 (2018).
16. Schlom, D. G., Chen, L.-Q., Pan, X., Schmehl, A. & Zurbuchen, M. A. A thin film approach to engineering functionality into oxides. *J. Am. Ceram. Soc.* **91**, 2429–2454 (2008).
17. Bhattacharya, A. & May, S. J. Magnetic oxide heterostructures. *Annu. Rev. Mater. Res.* **44**, 65–90 (2014).
18. Boschker, H. & Mannhart, J. Quantum-matter heterostructures. *Annu. Rev. Condens. Matter Phys.* **8**, 145–164 (2017).
19. Haraguchi, Y. et al. Magnetic ordering with an XY-like anisotropy in the honeycomb lattice iridates ZnIrO₃ and MgIrO₃ synthesized via a metathesis reaction. *Phys. Rev. Materials* **2**, 054411 (2018).
20. Haraguchi, Y. & Aruga Katori, H. Strong antiferromagnetic interaction owing to a large trigonal distortion in the spin-orbit-coupled honeycomb lattice iridate CdIrO₃. *Phys. Rev. Materials* **4**, 044401 (2020).
21. Toyosaki, H., Kawasaki, M. & Tokura, Y. Atomically smooth and single crystalline MnTiO₃ thin films with a ferrotoroidic structure. *Appl. Phys. Lett.* **93**, 072507 (2008).
22. Miura, K., Fujiwara, K., Shiogai, J., Nojima, T. & Tsukazaki, A. Electrical detection of the antiferromagnetic transition in MnTiO₃ ultrathin films by spin Hall magnetoresistance. *J. Appl. Phys.* **127**, 103903 (2020).
23. Kim, E. S. & Jeon, C. J. Microwave dielectric properties of A₂TiO₃ (A = Ni, Mg, Co, Mn) ceramics. *J. Eur. Ceram. Soc.* **30**, 341–346 (2010).
24. Pennycook, S. J. & Boatner, L. A. Chemically sensitive structure-imaging with a scanning transmission electron microscope. *Nature* **336**, 565–567 (1988).
25. Calvert, C. C., Rainforth, W. M., Sinclair, D. C. & West, A. R. Characterisation of grain boundaries in CaCu₃Ti₄O₁₂ using HREM, EDS and EELS. *J. Phys.: Conf. Ser.* **26**, 65–68 (2006).
26. Moatti, A., Sachan, R., Gupta, S. & Narayan, J. Vacancy-driven robust metallicity of structurally pinned monoclinic epitaxial VO₂ thin films. *ACS Appl. Mater. Interfaces* **11**, 3547–3554 (2019).
27. Matsuhiro, K. et al. Metal–insulator transition in pyrochlore iridates Ln₂Ir₂O₇ (Ln = Nd, Sm, and Eu). *J. Phys. Soc. Jpn.* **76**, 043706 (2007).

28. Cao, G. et al. Non-Fermi-liquid behavior in nearly ferromagnetic SrIrO_3 single crystals. *Phys. Rev. B* **76**, 100402(R) (2007).
29. Jang, S. Y. et al. The electronic structure of epitaxially stabilized 5d perovskite $\text{Ca}_{1-x}\text{Sr}_x\text{IrO}_3$ ($x = 0, 0.5$, and 1) thin films: the role of strong spin-orbit coupling. *J. Phys.: Condens. Matter* **22**, 485602 (2010).
30. Hirata, Y. et al. Complex orbital state stabilized by strong spin-orbit coupling in a metallic iridium oxide IrO_2 . *Phys. Rev. B* **87**, 161111(R) (2013).
31. Takayama, T. et al. Spin-orbit coupling induced semi-metallic state in the 1/3 hole-doped hyper-kagome $\text{Na}_3\text{Ir}_2\text{O}_8$. *Sci. Rep.* **4**, 6818 (2014).
32. Fujioka, J. et al. Strong-correlation induced high-mobility electrons in Dirac semimetal of perovskite oxide. *Nat. Commun.* **10**, 362 (2019).
33. Kim, B. J. et al. Novel $J_{\text{eff}} = 1/2$ Mott state induced by relativistic spin-orbit coupling in Sr_2IrO_4 . *Phys. Rev. Lett.* **101**, 076402 (2008).
34. Schaffer, R., Lee, E. K.-H., Yang, B.-J. & Kim, Y. B. Recent progress on correlated electron systems with strong spin-orbit coupling. *Rep. Prog. Phys.* **79**, 094504 (2016).
35. Nakayama, H. et al. Spin Hall magnetoresistance induced by a nonequilibrium proximity effect. *Phys. Rev. Lett.* **110**, 206601 (2013).
36. Schlitz, R. et al. Evolution of the spin hall magnetoresistance in $\text{Cr}_2\text{O}_3/\text{Pt}$ bilayers close to the Néel temperature. *Appl. Phys. Lett.* **112**, 132401 (2018).
37. Iino, T. et al. Resistive detection of the Néel temperature of Cr_2O_3 thin films. *Appl. Phys. Lett.* **114**, 022402 (2019).
38. Lebrun, R. et al. Anisotropies and magnetic phase transitions in insulating antiferromagnets determined by a spin-Hall magnetoresistance probe. *Commun. Phys.* **2**, 50 (2019).
39. Stickler, J. J., Kern, S., Wold, A. & Heller, G. S. Magnetic resonance and susceptibility of several ilmenite powders. *Phys. Rev.* **164**, 765 (1967).
40. Abarra, E. N., Takano, K., Hellman, F. & Berkowitz, A. E. Thermodynamic measurements of magnetic ordering in antiferromagnetic superlattices. *Phys. Rev. Lett.* **77**, 3451–3454 (1996).
41. Park, S. et al. Strain control of Morin temperature in epitaxial $\alpha\text{-Fe}_2\text{O}_3$ (0001) film. *EPL* **103**, 27007 (2013).
42. Pati, S. P., Al-Mahdawi, M., Ye, S., Shiokawa, Y., Nozaki, T. & Sahashi, M. Finite-size scaling effect on Néel temperature of antiferromagnetic Cr_2O_3 (0001) films in exchange-coupled heterostructures. *Phys. Rev. B* **94**, 224417 (2016).
43. Liu, J. et al. Heterointerface engineered electronic and magnetic phases of NdNiO_3 thin films. *Nat. Commun.* **4**, 2714 (2013).
44. King, P. D. C. et al. Atomic-scale control of competing electronic phases in ultrathin LaNiO_3 . *Nat. Nanotechnol.* **9**, 443–447 (2014).
45. Bovo, L., Rouleau, C. M., Prabhakaran, D. & Bramwell, S. T. Phase transitions in few-monolayer spin ice films. *Nat. Commun.* **10**, 1219 (2019).
46. Wulferding, D., Choi, Y., Lee, W. & Choi, K.-Y. Raman spectroscopic diagnostic of quantum spin liquids. *J. Phys.: Condens. Matter* **32**, 043001 (2020).
47. Cornelissen, L. J., Liu, J., Duine, R. A., Youssef, J. B. & van Wees, B. J. Long-distance transport of magnon spin information in a magnetic insulator at room temperature. *Nat. Phys.* **11**, 1022 (2015).
48. Lebrun, R. et al. Tunable long-distance spin transport in a crystalline antiferromagnetic iron oxide. *Nature* **561**, 222 (2018).
49. Koga, A., Minakawa, T., Murakami, Y. & Nasu, J. Spin transport in the quantum spin liquid state in the $S = 1$ Kitaev model: role of the fractionalized quasiparticles. *J. Phys. Soc. Jpn.* **89**, 033701 (2020).
50. Minakawa, T., Murakami, Y., Koga, A. & Nasu, J. Majorana-mediated spin transport in Kitaev quantum spin liquids. *Phys. Rev. Lett.* **125**, 047204 <https://journals.aps.org/prl/abstract/10.1103/PhysRevLett.125.047204> (2020).
51. Momma, K. & Izumi, F. VESTA 3 for three-dimensional visualization of crystal, volumetric and morphology data. *J. Appl. Cryst.* **44**, 1272–1276 (2011).

Acknowledgements

The authors are grateful to K. Harata, S. Ito and N. Saito for their experimental supports, Y. Motome for the stimulating discussions, and NEOARK Corporation for the use of the maskless lithography system PALET. This work was performed under the Inter-University Cooperative Research Program of the Institute for Materials Research, Tohoku University, Japan (Proposal No. 19G0410). This work was supported by JST CREST (JPMJCR18T2) and JSPS KAKENHI (15H058053 and 19H02423). K.N., R.I. and N.S. acknowledge support received from JSPS KAKENHI (19H05788) and the Research Hub for Advanced Nano Characterisation (No. 12024046) by MEXT, Japan.

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

Supplementary information is available for this paper at <https://doi.org/10.1038/s43246-020-00059-1>.

Correspondence and requests for materials should be addressed to K.F.

Reprints and permission information is available at <http://www.nature.com/reprints>

Publisher's note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made. The images or other third party material in this article are included in the article's Creative Commons license, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons license and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this license, visit <http://creativecommons.org/licenses/by/4.0/>.

© The Author(s) 2020