Unveiling unconventional magnetism
at the surface of Sr$_2$RuO$_4$

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Abstract

Materials with strongly correlated electrons exhibit physical properties that are often difficult to predict as they result from the interactions of large numbers of electrons combined with several quantum degrees of freedom. The layered oxide perovskite Sr$_2$RuO$_4$ is a strongly correlated electron material that has been intensively investigated since its discovery due to its unusual physical properties. Whilst recent experiments have reopened the debate on the exact symmetry of the superconducting state in Sr$_2$RuO$_4$, a deeper understanding of the Sr$_2$RuO$_4$ normal state appears crucial as this is the background in which electron pairing occurs. Here, by using low-energy muon spin spectroscopy we discover the existence of magnetism at the surface of Sr$_2$RuO$_4$ in its normal state. We detect static weak dipolar fields yet manifesting below a relatively high onset temperature larger than 50 K, which reveals the unconventional nature of the observed magnetism. We relate the origin of this phase breaking time reversal symmetry to electronic ordering in the form of orbital loop currents that originate at the reconstructed Sr$_2$RuO$_4$ surface. Our observations set a reference for the discovery of the same magnetic phase in other materials and unveil an electronic ordering mechanism that can influence unconventional electron pairing with broken time reversal symmetry in those materials where the observed magnetic phase coexists with superconductivity.
Main

Electronic ordering in condensed matter systems often occurs as a result of a phase transition, meaning that it involves a symmetry breaking. A classic example of the spontaneous breaking of time reversal symmetry is ferromagnetism, which originates from long-ranged ordering of electrons’ spins.

In systems of reduced dimensionality like two-dimensional (2D) materials, the increase in quantum fluctuations compared to three-dimensional (3D) systems can induce symmetry-breaking phase transitions and quantum orders that do not have a 3D equivalent\(^1\). The emergence of topological phase transitions in 2D solids and 2D superfluids in the absence of standard long-range ordering was first proposed by Kosterlitz and Thouless\(^3\), for which they were awarded the Nobel prize in 2016.

3D layered single crystals are the closest 3D analogue to 2D materials, since electronic correlations in these crystals mainly develop inside the plane of each layer and the electrons’ propagation is reduced along the crystal axis perpendicular to the layers. In layered single crystal oxide perovskites, the dominance of in-plane correlations between electrons of the \(d\) orbitals often results in the emergence of exotic phases\(^4\), some of which have been discovered over the past thirty years like high-temperature superconductivity\(^5\), metal-to-insulator transitions\(^6\) and multiferroicity\(^7\).

\(\text{Sr}_2\text{RuO}_4\) (SRO\(_{214}\)) is a peculiar oxide perovskite on the verge of various electronic instabilities that can be further stabilized by the asymmetry that the SRO\(_{214}\) surface exhibits compared to the bulk, as result of a structural reorganization of its surface RuO\(_6\) octahedra. Apart from intense studies\(^1,8,9,10\) aiming at determining the nature of the superconducting symmetry in SRO\(_{214}\), which remains under debate, evidence for spin fluctuations\(^11\) or magnetism under uniaxial pressure\(^12\) has also been reported for SRO\(_{214}\) single crystals in the normal state. These investigations, however, do not provide any information about the SRO\(_{214}\) surface selectively but rather focus on the SRO\(_{214}\) bulk properties.

At the surface of SRO\(_{214}\), it has been theoretically suggested that conventional ferromagnetic ordering can emerge possibly stabilized by the rotation of the surface RuO\(_6\) octahedra\(^13\), but definitive evidence for the existence of magnetism at the SRO\(_{214}\) surface has never been demonstrated, not even with scanning superconducting quantum interference device (SQUID) magnetometry\(^14\). Angle-resolved photoemission spectroscopy measurements on SRO\(_{214}\) also reveal the presence of surface states\(^15\), but the correlation between these surface states and magnetism is not conclusive\(^16\).

Here, by using the extremely high sensitivity of low-energy muon spin spectroscopy (LE-\(\mu\)SR) to magnetic fields and its nanometre depth resolution\(^17,18\), we find unambiguous evidence for the existence of an unconventional magnetic phase near the surface of SRO\(_{214}\) single crystals. The hallmark features of the magnetic phase that we unveil in SRO\(_{214}\) are a relatively high temperature onset (\(T_{\text{on}}\)) between 50 K and 75 K associated with a small amplitude of the magnetic moment.

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(< 0.01 \mu_B/Ru atom, with \( \mu_B = 9.27 \times 10^{-24} \) J T\(^{-1}\) being the Bohr magneton), a homogeneous distribution of the sources of magnetism within the \( ab \)-plane of the SRO\(_{214}\) crystals, and a decay in intensity of the magnetic signal from the SRO\(_{214}\) surface over a length scale of \( \sim 10\)-20 nm. The features of this magnetic phase suggest that it cannot be reconciled with conventional ferromagnetism. We show instead that spin-orbital entanglement of the electronic states at the Fermi level results in orbitally frustrated loop currents within the surface RuO\(_6\) octahedra, which can generate the unconventional magnetism that we detect.

**Evidence for surface magnetism**

We perform LE-\( \mu \)SR measurements on SRO\(_{214}\) single crystals grown by the floating zone method. The SRO\(_{214}\) crystals used in this experiment are highly pure and have superconducting critical temperature of \( \sim 1.45 \) K and residual resistivity ratio larger than 200, as evidenced by the X-ray diffraction and electronic transport measurements in Supplementary Fig. 1.

For the LE-\( \mu \)SR measurements, the crystals are cleaved with a non-magnetic ZrO\(_2\) razor blade to avoid contamination from magnetic impurities and arranged to form a mosaic of size comparable to that of the muon beam (\( \sim 2 \) cm in diameter) to maximize the amplitude of the signal (Fig. 1a). We perform most of the LE-\( \mu \)SR measurements with an external magnetic field (\( B_{ext} \)) applied out-of-plane (i.e., along the c-axis of SRO\(_{214}\)) defined as the z-axis of our orthonormal reference-axes system (Fig. 1b). The LE-\( \mu \)SR data are collected in two different configurations, namely both with the initial muon spin polarization (\( S_{\mu^+} \)) oriented perpendicular to \( B_{ext} \), known as transverse-field (TF) configuration, and with \( S_{\mu^+} \) collinear to \( B_{ext} \), known as longitudinal-field (LF) configuration (Fig. 1c). We also carry out zero-field (ZF) measurements in the same setup adopted for LF but with \( B_{ext} = 0 \), as shown in Fig. 1c.

To determine the presence of any magnetism in SRO\(_{214}\) and study its temperature (\( T \)) and depth dependence, we first perform LE-\( \mu \)SR temperature scans (\( T \)-scans) in the TF configuration as a function of energy (\( E \)). In the TF setup, the muons implanted with energy \( E \) precess about the perpendicular \( B_{ext} \) at an average frequency \( \omega_s(E) = \gamma_\mu B_{1oc}(E) \) with \( \gamma_\mu = 851.616 \) MHz T\(^{-1}\) being the muon’s gyromagnetic ratio. Each \( E \) corresponds to a different muon implantation depth profile, \( z(E) \), simulated using the Monte Carlo algorithm TrimSP\(^{19}\) as shown in Fig. 1d.

The \( T \)-scans are carried out whilst warming up the SRO\(_{214}\) crystals, after zero-field cooling (ZFC) them and applying \( B_{ext} = 100 \) Gauss at the lowest \( T \). For the analysis of the \( T \)-scans in TF, we model the asymmetry signal \( A_S(t) \) as \( A_0 e^{-\lambda t} \cos[\gamma_\mu B_{1oc} t + \phi_0] \), where \( \lambda \) is the muon spin depolarization rate, which is proportional to the width of the local field distribution with average \( B_{1oc} \) sensed by
muons, $A_0$ is the initial asymmetry which depends on the initial $S_\mu^+$, and $\varphi_0$ is the initial phase depending on the initial $S_\mu^+$ and on the detectors geometry (see Supplementary Information). We note that the finite width of the muons’ implantation profiles in LE-μSR (Fig. 1d) leads to a broadening of the field distribution experienced by the muons implanted at a given $E$. As a result, the asymmetry signal is better fitted assuming an exponential rather than a Gaussian relaxation rate, which is instead typically used in bulk-μSR studies where all muons implanted in a homogeneous sample experience the same field distribution. At a given $E$, we also perform a global fit\textsuperscript{20} including all the data points collected as a function of $T$ and assuming $A_0$ and $\varphi_0$ as $T$-independent, since $A_0$ and $\varphi_0$ are both related to the initial $S_\mu^+$ which is $T$-independent.

Fig. 1: Low energy μSR setup for measurements on SRO$_{214}$ single crystals. a, SRO$_{214}$ crystals cleaved and glued onto a Ni-coated aluminium plate to form a mosaic for the LE-μSR measurements. b, Experimental LE-μSR setup with applied $B_{\text{ext}}$ perpendicular to the sample (i.e., along the $c$-axis of SRO$_{214}$) and arrays of positron detectors used to count muon decay events. The schematic cut-out allows to view the sample inside the detectors. c, LE-μSR measurement configurations for different initial muon spin polarization $S_\mu^+$: $S_\mu^+$ perpendicular to $B_{\text{ext}}$ and precessing in the $xy$-plane as indicated by the shadowed red circle (transverse field, top) or $S_\mu^+$ collinear to $B_{\text{ext}}$ (longitudinal field or zero field with $B_{\text{ext}} = 0$, bottom). d, Muon implantation profiles in SRO$_{214}$ simulated for a few representative implantation energies.
The results of the analysis are shown in Fig. 2, where we plot for each $E$ the $T$ dependence of the shift in $\lambda$, $\Delta \lambda(T)$, from the $\lambda$ measured at the highest $T$ ($\sim 270$ K in Fig. 2). The analysis of $\Delta \lambda$ allows to remove systematic effects such as variable contributions to $\lambda$ due the measurement background.

An increase in $\Delta \lambda$ as $T$ is decreased signifies a broadening in the distribution of local fields experienced by muons at their implantation sites, and therefore it is a signature of enhanced magnetism emerging in the SRO$_{214}$ crystals as they are cooled down. Fig. 2 shows that $\Delta \lambda$ increases as $T$ is lowered at all $E$s investigated, with a more pronounced increase in $\Delta \lambda$ occurring closer to the SRO$_{214}$ crystals’ surface at $E = 3$ keV corresponding to an average muon stopping depth $\bar{z} \sim 15$ nm.

![Fig. 2: Temperature dependence of magnetism in SRO$_{214}$ at different implantation depths. Shift in muon depolarization rate, $\Delta \lambda$, from the $\lambda$ value measured at $T = 270$ K as a function of temperature $T$ measured in a TF setup (inset) with $B_{\text{ext}} = 100$ Gauss at different implantation energy $E$ values. The solid grey line serves as guide to the eye and marks the $T$ range (grey shaded region) where $\Delta \lambda$ changes slope for $E = 3$ keV, which we identify as the onset temperature $T_{\text{on}}$ of the magnetism in SRO$_{214}$.](image)

(\$\bar{z}$ values are determined from the stopping profiles in Fig. 1d). The $\Delta \lambda$ values reported in Fig. 2, in combination with the corresponding raw asymmetry profiles with corresponding fits reported in the Supplementary Information, show that $\Delta \lambda$ at $E = 3$ keV significantly changes slope at a $T$ between 50 K and 75 K, which we identify as the $T_{\text{on}}$ of the magnetism. The data sets in Fig. 2 and Supplementary Fig. 7 for $E = 6$ keV and $E = 14$ keV also demonstrate that the onset temperature $T_{\text{on}}$ of the magnetism detected by muons decreases at higher implantation depths, since $\Delta \lambda$ for $E \geq 6$ keV does not change significantly until a $T \sim 25$ K is reached, which is lower than the estimated $50$ K $< T_{\text{on}} < 75$ K. This result further confirms the surface nature of the magnetism that we measure in SRO$_{214}$ because the muons implanted deeper inside SRO$_{214}$ only experience an increase in their depolarization rate when
the magnetism on the surface has become sufficiently strong, which occurs when $T$ has been decreased well below the onset of the magnetic phase transition at $T_{on}$.

We note that we have verified the reproducibility of the results reported in Fig. 2 and measured the same trends for $\Delta \lambda$ in two different batches of SRO$_{214}$ crystals, which demonstrates that the observed magnetism is an intrinsic property of SRO$_{214}$. The LE-\(\mu\)SR data on these two different batches of SRO$_{214}$ crystals have been collected over three beamtime sessions with various cryostats and magnets, which also rules out other possible artefacts related to the measurement setup. We confirm the emergence of magnetism from the $T$-dependence of $\Delta \lambda$ at different $E$ values also for a different TF configuration, where $B_{ext}$ is applied in-plane other than out-of-plane.

**Field and depth dependence of magnetism**

To further characterize the nature of the magnetic states observed in SRO$_{214}$, we study the response of these states in a higher applied $B_{ext} = 1500$ Gauss in the TF setup (Fig. 3a, b). Although we do not observe significant variations of $B_{loc}$ with $T$ when $B_{ext} = 100$ Gauss, Fig. 3a shows that with $B_{ext} = 1500$ Gauss, $B_{loc}$ increases as $T$ is lowered for both $E = 3$ keV and $E = 14$ keV, before eventually decreasing in amplitude for $T < 25$ K. We also find that $B_{loc}$ at $E = 3$ keV deviates from that measured at $E = 14$ keV through exhibiting a positive shift from the latter for $T < 25$ K (Fig. 3a).

The $B_{loc}$ curves in Fig. 3a are reminiscent of the Knight shift determined by nuclear magnetic resonance$^{11}$ in SRO$_{214}$ – which is a measure of the local susceptibility or density of states of the material near the Fermi surface. The positive shift in $B_{loc}$ at $E = 3$ keV compared to $E = 14$ keV at $T < 25$ K (Fig. 3a) can therefore be correlated to an increase in the susceptibility based on the results in ref. $^{11}$, which is consistent with a strengthening of magnetism near the SRO$_{214}$ surface. The data in Fig. 3b also indicate that that $\Delta \lambda$ in $B_{ext} = 1500$ Gauss exhibits a clear increase at $E = 3$ keV within the same $T$ range reported in Fig. 2.

To determine the depth range of the magnetism whilst moving from the surface to the bulk of SRO$_{214}$, we perform energy scans ($E$-scans) for two different $B_{ext}$ values (100 and 1500 Gauss). In Fig. 3c, d we report the depth variation of the shifts in $B_{loc}$, $\Delta B_{loc}$, and $\Delta \lambda$ between $T = 5$ K and $T_{on}$ measured for $B_{ext} = 100$ and 1500 Gauss. Although $\Delta B_{loc}$ versus $E$ is $\sim 0$ for $B_{ext} = 100$ Gauss, in a higher applied $B_{ext} = 1500$ Gauss we observe an increase in $\Delta B_{loc}$ for $E < 4$ keV up to $-0.65$ Gauss (corresponding to $-0.45\%$ of $B_{ext}$). This result suggests that a $\Delta B_{loc}$ increase can also be present for $B_{ext} = 100$ Gauss, but it may not be resolved, as it would fall within the experimental noise level. For both $B_{ext}$ values, $\Delta \lambda$ increases for $E < 4$ keV (Fig. 3d), meaning that, as the samples are cooled down, the magnetic signal probed by muons becomes stronger only up to an average implantation depth $\bar{z}$ of $\sim 20$ nm from the surface of the SRO$_{214}$ crystals ($\bar{z}$ is determined from the simulated stopping
profiles in Fig. 1d). This result also rules out magnetic impurities as the possible origin for the observed magnetic states because any magnetic impurities, if present, should not always be localized close to the surface of randomly cleaved SRO$_{214}$ crystals.

We note that a paramagnetic Knight shift in the $^{17}$O nuclear magnetic resonance (NMR) signal has been recently measured for SRO$_{214}$ in its normal state under uniaxial strain$^{21}$. The NMR Knight shift is of ~ 100 Gauss in an applied field of $8 \times 10^4$ Gauss, and it exhibits an anomalous enhancement related to spin fluctuations at the critical strain $\varepsilon_v$, defined as the strain value where the Fermi level reaches the Van Hove singularity (VHS). We note that in our experiment, the Fermi level of the SRO$_{214}$ surface layers is not at the VHS and the layers underneath are just bulk-like as demonstrated.
by previous angle-resolved photoemission spectroscopy (ARPES) measurements\textsuperscript{22,23}, whilst in ref. \textsuperscript{21} the authors reach the VHS through the application of $\varepsilon_v$. Despite these dissimilarities between the two experiments, one can argue that the surface of SRO\textsubscript{214} has a different local strain compared to the bulk, meaning that there may exist a correlation between our $\Delta B_{\text{loc}}$ enhancement at the SRO\textsubscript{214} surface and the Knight shift. Drawing a quantitative comparison between our $\Delta B_{\text{loc}}$ enhancement and Knight shift, however, is difficult for several reasons. First, as discussed in ref. \textsuperscript{21}, the Knight shift includes several contributions which cannot be fully separated and it is specifically measured for the oxygen sites, whilst the muon stopping sites do not simply coincide with the oxygen sites, meaning that the interaction of the muons with SRO\textsubscript{214} is different. Second, our $\Delta B_{\text{loc}}$ shift ($\sim 0.2$ Gauss in a field of 1500 Gauss) is smaller than the Knight shift reported in ref. \textsuperscript{21} by several orders of magnitudes, and it is measured in different experimental conditions from those of the NMR experiment, which cannot be reproduced in the LE-$\mu$SR setup where neither larger magnetic field than those used, nor strain can be applied. These factors make it difficult to determine if and to which extent the shift in $\Delta B_{\text{loc}}$ would increase if the LE-$\mu$SR measurements could be done using similar settings to the NMR measurements. Last, even if we cannot exclude that a correlation between the NMR Knight shift and $\Delta B_{\text{loc}}$ exists, our LE-$\mu$SR measurements suggest that the $\Delta B_{\text{loc}}$ is characterized by different experimental signatures from those reported in ref. \textsuperscript{21} for paramagnetic Knight shift because $\Delta B_{\text{loc}}$ originates from an ordered phase that breaks time reversal symmetry and that is also static in nature, as evidenced by our ZF measurements reported below.

**Static nature and weakness of magnetism**

We also perform measurements in a LF/ZF configuration to gain further insights into the nature of the magnetism observed in SRO\textsubscript{214} and in particular to determine whether the enhancement in $\Delta \lambda$ close to the SRO\textsubscript{214} surface for $T < T_{\text{on}}$ (Fig. 2) is due to an increase in static magnetic fields or to a reduction in spin fluctuations as $T$ decreases.

The measurements performed in the LF/ZF configurations demonstrate that the magnetism in SRO\textsubscript{214} is not related to spin fluctuations, but it rather has a static nature. We fit the LF/ZF asymmetry data to an exponential/Lorentzian Kubo-Toyabe function\textsuperscript{24} (see also Supplementary Information).

Fig. 4 shows that the damping in the asymmetry is decoupled as $B_{\text{ext}}$ is progressively increased from $B_{\text{ext}} = 0$ (ZF) to $B_{\text{ext}} = 100$ Gauss (LF) for both directions of the collinear alignments of $S_{\mu^+}$ with $B_{\text{ext}}$. The results clearly indicate that the local magnetic dipolar fields are static and of the order of $\sim 10$ Gauss. If the asymmetry damping were instead due to magnetic fluctuations of the electronic moments, meaning due to spin lattice relaxation, a $B_{\text{ext}}$ of $\sim 10$ Gauss would not affect the spin lattice.
relaxation since the exchange energy due to Zeeman splitting in a field of ~ 10 Gauss is much smaller than the thermal energy at $T = 5$ K.

To quantify the intensity of the static magnetism that we detect, we note that spin polarized positive muons used in this experiment are likely to implant closer to an oxygen atom with the SRO$_{214}$ unit cell, due to the higher electron affinity of O compared to Ru. Since the Ru-O atomic bond length is ~ 2 Å in SRO$_{214}$ (ref. 25), we estimate that the magnetic dipolar fields probed by muons at their implantation site (~ 10 Gauss; Fig. 4) correspond to a magnetic moment much smaller than 0.01 $\mu_B$/Ru. atom.

Analysis and discussion

To summarize our experimental findings, we detect a magnetic phase with $50 \, K < T_{on} < 75 \, K$ (Fig. 2 and Fig. 3b) and localized within the first 10-20 nm from the SRO$_{214}$ surface (Fig. 3d), which induces a positive $\Delta B_{loc}$ shift near the surface only in higher $B_{ext}$ combined with a positive $\Delta \lambda$ shift independent on $B_{ext}$ (Fig. 3c, d). The magnetic phase detected is not related to fluctuations, but it is static in nature and it corresponds to an average magnetic moment experienced by muons of less than 0.01 $\mu_B$/Ru atom at their implantation sites (Fig. 4). Based on these results, we can rule out several possibilities for the magnetic phases since they cannot account for our experimental observations.

The small magnitude of the moment in combination with the relatively high $T_{on}$ suggest that the magnetic phase detected at the SRO$_{214}$ surface is incompatible with conventional ferromagnetism. Ab-initio calculations indeed show that conventional ferromagnetic ordering of the Ru moments stabilized by the RuO$_6$ octahedra rotation at the SRO$_{214}$ surface would result in an exchange energy
due to Zeeman splitting of \( \sim 1 \) eV, which corresponds to a magnetic moment of \( \sim 1 \mu_B/\text{Ru atom} \). Conventional ferromagnetism due to surface RuO\(_6\) octahedra distortion, which are present in our SRO\(_{214}\) crystals after cleavage as confirmed by the low-energy electron diffraction measurements (LEED) in Supplementary Fig. 2, therefore cannot account for our LE-\(\mu\)SR results.

Similarly, single-unit-cell thick SrRuO\(_3\) (SRO\(_{113}\)), which is the parent ferromagnetic compound of SRO\(_{214}\), has a magnetic moment (\( \sim 0.2 \mu_B/\text{Ru atom} \), ref. 26) that is a couple of orders of magnitudes larger than that probed by muons in our experiment and which can be detected by scanning SQUID magnetometry\(^{26}\). Supplementary Fig. 3 shows that scanning SQUID measurements performed by our group on the same crystals used for LE-\(\mu\)SR experiments cannot resolve any magnetic flux originating from SRO\(_{214}\), which also rules out the presence of SRO\(_{113}\) or other magnetic impurities in our SRO\(_{214}\) samples, consistently with the depth dependence of magnetism in Fig. 3c, d. We note that, in our scanning SQUID measurements, we can only detect small magnetic spots on the SRO\(_{214}\) crystals (Supplementary Fig. 3), most likely of extrinsic origin and possibly introduced during the cleaving process. These magnetic spots, however, only occupy a very small area of the sample surface (much less than 1\%) and therefore they would only affect a small fraction of the implanted muons, meaning that they cannot account for the uniform increase in the depolarization rate measured in the LE-\(\mu\)SR signal below \( T_{\text{on}} \). The results obtained by scanning SQUID therefore further confirm that the magnetic signal which we resolve by LE-\(\mu\)SR in SRO\(_{214}\) has to be intrinsic of the material and it is associated to a magnetic moment below the typical moment values expected for conventional ferromagnetism.

Further to conventional ferromagnetism, we also rule out magnetism due to spin textures with cancelling moments\(^{27,28}\) or to correlations between spurious magnetic impurities as possible explanation for our results in SRO\(_{214}\). This is because the appearance of such magnetic phases due to long-ranged correlations between magnetic spins or magnetic impurities embedded into a metallic Fermi sea at the relatively high onset temperature \( 50 \text{ K} < T_{\text{on}} < 75 \text{ K} \) we measure would require a large strength of the Ruderman-Kittel-Kasuya-Yosida interaction and/or a strong crystal field anisotropy. This should, however, should result in a magnetic moment much larger than the value that we measure (much less than 0.01 \( \mu_B/\text{Ru atom} \)).

We also exclude magnetic phases with antiferromagnetic ordering marked by a vanishing net magnetization and competing dipolar fields. This is because the SRO\(_{214}\) is layered and tetragonal, and therefore has inequivalent distances between the in-plane neighbouring magnetic moments and the moments in adjacent RuO\(_2\) planes. As a result, a muon implanted inside SRO\(_{214}\) in any energetically favourable sites, for instance close to an apical oxygen due to its electrical affinity, would very unlikely experience an almost vanishing dipolar moment. Indeed, in ruthenates with
antiferromagnetic properties, the $B_{\text{loc}}$ probed by muons corresponds to moments much larger than 0.01 $\mu_B$/Ru atom.\(^{29}\)

In addition to the above features, we also note that the time-reversal symmetry breaking (TRSB) normal (i.e., non-superconducting) phase that we detect at the SRO\(_{214}\) surface has to be homogenously distributed within the $ab$-plane of the SRO\(_{214}\) due to the monomodal $p(B_{\text{loc}})$ distribution. The magnetism sources should also correlate over a length scale comparable with the size of a single unit cell and be consistent with the SRO\(_{214}\) translational symmetry. This is because the signal measured at a given $E$ is the sum of the contributions from all the muons implanted at $\tilde{z}(E)$ in any position within the $ab$-plane of the SRO\(_{214}\) crystals.

Possible unconventional normal-state TRSB phases which would meet the above requirements and generate weak static magnetic dipolar fields in the absence of long-ranged ferromagnetic ordering include intra-unit cell spin nematicity and electronic loop currents, like those reported for other materials including iron-based superconductors\(^{30,31}\), iridates\(^{32}\) and cuprates\(^{33,34}\). The existence of a spin-nematic phase at the SRO\(_{214}\) surface, however, can be excluded on the basis of symmetry considerations because a spin-nematic phase does not break inversion symmetry\(^{35}\), and therefore it would be energetically unfavoured by the inversion asymmetric interactions occurring at the SRO\(_{214}\) surface\(^{36}\).

Our theoretical analysis reported below shows that the origin of the normal-state TRSB phase probed on the surface of SRO\(_{214}\) can be ascribed to an orbital loop current with staggered magnetic flux. This orbital loop current phase is similar to that proposed to explain the intra-unit-cell antiferromagnetism in the pseudogap state of underdoped cuprates like YBa\(_2\)Cu\(_3\)O\(_{6+\delta}\) and HgBa\(_2\)CuO\(_{4+\delta}\) (refs.\(^{37,38}\)). The existence of an orbital loop current phase in cuprates, however, remains still controversial not only because earlier experimental evidence supporting the existence of this phase, and mostly based on spin-polarized neutrons\(^{37,38}\), has not been confirmed by more recent studies, but also because alternative phases like charge density waves or spin density waves can equally account for the formation of the pseudogap in the normal state\(^{39,40}\). Similarly, for materials like iron-based superconductors, it is difficult to demonstrate conclusive evidence for an orbital loop current phase based on experiments demonstrating evidence for TRSB in the normal state because of the simultaneous presence of a TRSB spin density wave in the same materials\(^{41}\). To the best of our knowledge and as reported in ref.\(^{42}\), the only two material systems for which evidence for an orbital loop current phase has been reported without effects that can be related to other coexisting TRSB phases include the Mott insulator Sr\(_2\)IrO\(_4\) using non-linear optical microscopy\(^{43}\) and the two-leg ladder cuprate Sr\(_{14-x}\)Ca\(_x\)Cu\(_{24}\)O\(_{21}\) using spin-polarized neutrons\(^{44}\). Spin-polarized neutron studies,
however, have not confirmed the presence of normal-state TRSB orbital loop currents in Sr$_2$IrO$_4$ (ref. 43), whilst the orbital loop current phase reported for Sr$_{14-x}$Ca$_x$Cu$_{24}$O$_{21}$ cannot be directly correlated to that which we propose for SRO$_{214}$, since Sr$_{14-x}$Ca$_x$Cu$_{24}$O$_{21}$ has radically different physical properties in that it is non-superconducting and behaves like a spin liquid above a certain hole doping.

**Orbital loop current phase**

To understand the physical mechanism underlying the magnetism measured in SRO$_{214}$, we consider orbital loop currents emerging as a result of electronic instabilities at the Fermi level. We use a tight-binding description of the electronic structure of SRO$_{214}$ including $d$-orbitals at the Ru sites and $p$-orbitals at the planar O sites and consider $d$-$p$ and $p$-$p$ Coulomb interactions as responsible for the electronic instabilities yielding the orbital loop current phase (Fig. 5a).

Inversion symmetry breaking at the SRO$_{214}$ surface rules out an orbital loop current phase that is spatially symmetric like that consisting of orbital currents flowing along each bond of the RuO$_4$ plaquette (see Supplementary Information). Based on symmetry considerations, we therefore restrict our analysis to magnetic phases originating from asymmetric orbital loop currents, namely combinations of clockwise and anticlockwise orbital currents generating opposite magnetic fluxes only within two sections of the RuO$_4$ plaquette (Fig. 5a) and determine whether this type of phase is consistent with the features of the magnetism observed in SRO$_{214}$.

For a given RuO$_4$ plaquette, there are two possible asymmetric TRSB loop current phases which differ by the way loop currents are distributed for the $d_{xy}$ and ($d_{xz}$, $d_{yz}$) orbitals sectors (Fig. 5b). Asymmetric loop current phases of several neighbouring plaquettes must combine at the SRO$_{214}$ surface compatibly with the rotation of the RuO$_6$ octahedra to yield the loop current distribution for a SRO$_{214}$ supercell. The net loop current distribution in the SRO$_{214}$ supercell has also to result in staggered magnetic fluxes to prevent spontaneous current flow or charge accumulation, the existence of which is not possible in the metallic state of SRO$_{214}$.

A first result which we obtain from our calculations is that the magnetic phase originating from orbital loop currents flowing inside the SRO$_{214}$ supercell can indeed be the ground state of SRO$_{214}$ because it is characterized by a lower free energy compared to the non-magnetic SRO$_{214}$ configuration. We also find that this unconventional orbital loop current (LC) phase can stabilize into two different energy states, the degeneracy of which is lifted by spin-orbit coupling in SRO$_{214}$, depending on the distribution of the loop currents around the $d$-orbitals at the Ru sites. Fig. 5c shows that one of these two magnetic states is generated by loop currents having the same sign for the $d_{xy}$
and \((d_{xz}, d_{yz})\) orbitals at the Ru sites, here denoted as LC\(^+\) state, whilst the other state is generated by loop currents for the \(d_{xy}\) and \((d_{xz}, d_{yz})\) orbitals at the Ru sites having opposite sign (LC\(^-\) state).

Fig. 5: Magnetism due to orbital loop currents in SRO\(_{214}\). a, Illustration of the RuO\(_4\) plaquette and of the corresponding \(d\)-orbitals for the Ru atoms and \(p\)-orbitals for the O atoms with asymmetric loop current distributions generating magnetic flux pointing inward or outward the RuO\(_4\) plane. b, Possible orbital loop currents for a given RuO\(_4\) plaquette associated with the Ru-O hybridization of the \(d_{xy}\) orbitals (top) and of the \((d_{xz}, d_{yz})\) orbitals (bottom). c, Loop current states with equal (LC\(^+\) state) and opposite sign (LC\(^-\) state) of the magnetic flux associated with the \(xy\)- and \(z\)-orbital sectors of the RuO plaquettes in the SRO\(_{214}\) supercell. d, Free energy of the LC\(^+\) (dashed lines) and LC\(^-\) states (solid lines) calculated at \(T = 50\) K for different values of the \(d\)-\(p\) Coulomb interaction \(U\) in terms of the order parameter \(\phi\) setting the amplitude of the bond current.

A calculation of the free energy for the LC\(^-\) and LC\(^+\) states as a function of the Coulomb interaction \(U\) between electrons of the \(p\)- and \(d\)-orbitals of the O and Ru atoms for \(T\) below \(T_{on}\) shows that the LC\(^-\) state is energetically favourable compared to the LC\(^+\) state (Fig. 5d and Supplementary Information). Fig. 5d also shows that the free energy gain with respect to the normal state with zero flux is \(\sim 20\) - \(30\) meV which corresponds to a temperature of a few hundred Kelvins, which is of the same magnitude as \(T_{on}\). The order parameter \(\phi\) is the expectation value of the asymmetric bonding operator in SRO\(_{214}\) (see Supplementary Information).
We last verify that the orbital loop currents corresponding to the most stable LC- configuration are consistent with the strength of the magnetic field probed by muons near the SRO\textsubscript{214} surface. The magnetic field in the LC- configuration is obtained by determining the average current flowing along each bond inside the SRO\textsubscript{214} supercell and then deriving the net total field according to the Biot-Savart law. Using experimental values for the magnetic permeability of SRO\textsubscript{214}, $\mu_m \approx 2 \cdot 10^{-2}$ Gauss m$^{-1}$ A$^{-1}$ (ref. 11), and ab-initio values for the nearest-neighbour hopping parameters $t$ for the $d$- and $p$- orbitals$^{36,45}$, we obtain a $B_{\text{loc}}$ value in the range of 5 to 15 Gauss which is consistent with the order of magnitude measured experimentally by LE-$\mu$SR.

In conclusion, our study demonstrates clear evidence for the existence of an unconventional magnetic phase in the surface region of SRO\textsubscript{214}. We show that loop currents with vanishing net magnetic flux due to orbital frustration can account for the hallmark signatures of the observed TRSB phase at the SRO\textsubscript{214} surface. The orbital dependent nature of the loop current phase suggests that mechanisms lowering the crystalline symmetry, e.g. strain, can increase the orbital imbalance and result in stronger magnetism. From this point of view, our results can be linked to the strain-induced magnetism and other magnetic phenomena already observed$^{11,12,28}$ in the bulk of SRO\textsubscript{214}.

Another important implication of our results concerns the interplay between the normal-state TRSB phase, which we observe at the SRO\textsubscript{214} surface, and the TRSB existing in the superconducting state of SRO\textsubscript{214}. Although the spin-triplet nature of the superconducting order parameter in SRO\textsubscript{214} is still under debate, previous studies show that TRSB due the pairing correlations with intrinsic chirality$^{8,9,10,46}$ (i.e., spin-singlet $d_{xz} \pm id_{yz}$ or spin-triplet $p_x \pm ip_y$) is a hallmark feature of the superconductivity in SRO\textsubscript{214}. The normal-state TRSB due to orbital loop currents does not contradict the TRSB of the superconducting state in SRO\textsubscript{214}, but it can bring further insights into the mechanism responsible for pairing formation with intrinsic chirality. This is because fluctuations of normal-state orbital loop currents, which are chiral in nature (they flow both clockwise and anticlockwise within the SRO\textsubscript{214} supercell), may extend from the SRO\textsubscript{214} surface, where such orbital loop currents get pinned and ordered, deeper into the bulk of SRO\textsubscript{214} and provide an unusual electronic mechanism responsible for the formation of Cooper pairs with intrinsic chirality in SRO\textsubscript{214}.

A normal-state TRBS phase due to staggered orbital loop currents on the SRO\textsubscript{214} surface should in principle not favour the formation of a uniform superconducting phase in SRO\textsubscript{214} due to the incompatibility of the translation symmetry vectors of the two phases. Nevertheless, it is also possible that the superconducting order parameter in SRO\textsubscript{214} reconstructs and follows a non-uniform profile (e.g., a pair density wave profile) to accommodate the spatial variations of the orbital loop currents phase and minimize the magnetic fields associated with them, for example by driving pairing between
the $d_{xy}$ and $(d_{xz}, d_{yz})$ orbitals. Both scenarios, meaning the suppression or the reconstruction of the superconducting order parameter due to its competition with the normal-state TRSB loop current phase, would lead to a superconducting state at the surface different from bulk of SRO$_{214}$ – which can also account for some of the discrepancies between bulk-sensitive and surface-sensitive spectroscopy experiments reported to date on SRO$_{214}$.

Dipolar fields generated near edge dislocations, which are particularly relevant near the SRO$_{214}$ surface due to local strain inhomogeneities, can also be a source of time reversal symmetry breaking$^{47}$ and therefore further contribute to the discrepancy in the symmetry of the superconducting order parameter determined based on bulk- and surface-sensitive spectroscopy techniques.

It is interesting to observe that, regardless of the orbital loop current mechanism that we propose to explain the magnetism on the SRO$_{214}$ surface, this magnetism already represents a source of TRSB which can become more visible as superconductivity sets in, but without the TRSB being related to the superconducting order parameter per se. A normal-state TRSB phase can extend in principle to the entire sample as superconductivity sets in, if an increase in the characteristic length scale of magnetism along the direction normal to the SRO$_{214}$ surface takes place. For this scenario to occur, the magnetic moment at the SRO$_{214}$ surface should generate dipolar fields in the superconducting state that are stronger than the critical field $H_{c1}$ of SRO$_{214}$. It has been reported that $H_{c1}$ is of $\sim 10$ Gauss at $T = 0$ (ref. $^{48}$), meaning that $H_{c1}$ is of the same strength as the dipolar fields probed by muons in our experiment. The dipolar fields that we detect by LE-$\mu$SR at the SRO$_{214}$ surface can therefore in principle induce the formation of a vortex liquid phase like that described in ref. $^{48}$. This vortex liquid phase can give rise to a magnetic field distribution experienced by muons that is rather uniform, unlike the distribution corresponding to a vortex lattice, and possibly explain the TRSB in the superconducting state of SRO$_{214}$ reported in previous experiments based on bulk $\mu$SR$^{8,12}$.

Future studies will therefore have to clarify to which extent a normal-state TRSB phase at the surface can influence the superconducting state of SRO$_{214}$ and determine its symmetry and possible TRSB nature, since superconducting pairing must occur in the presence of a phase breaking time reversal symmetry already in the normal state. More generally, our results set a reference for the discovery of similar electronic phases in other compounds where orbital correlations play a role, and suggest a novel mechanism originating in the normal state that can result in the formation of unconventional superconducting pairing associated with time reversal symmetry breaking.
Methods

Sample preparation
The Sr$_2$RuO$_4$ (SRO$_{214}$) single crystals used in this experiment are grown by the floating zone method and cleaved with a non-magnetic ZrO$_2$ to avoid contamination from magnetic impurities. The cleaved pieces are glued onto a Ni-coated aluminium plate to form a mosaic for the low energy $\mu$SR measurements of size comparable to the muon beam (~ 2 cm in diameter).

Electronic transport and structural characterization
The electrical resistance of the SRO$_{214}$ crystals is measured in a four-probe configuration inside a cryogen-free system (Cryogenic Ltd.) with base temperature of ~ 0.3 K using a current-biased setup with current equal or less than 0.1 mA.

High-angle X-ray diffraction measurements on the same SRO$_{214}$ samples are performed using a Panalytical X-Pert MRD PRO diffractometer. The diffractometer is equipped with a monochromatic Cu $K_{\alpha 1}$ radiation with wavelength $\lambda = 0.154$ 056 nm obtained by a four-crystal Ge (220) asymmetric monochromator and a graded parabolic mirror positioned on the primary arm to the incident beam divergence to 0.12 arc sec. A triple axis module with triple axis detector is used for the diffracted beam.

Low-energy electron diffraction (LEED)
LEED measurements are carried out using a LEED spectrometer (SPECS) with electron energies of 185, 199 and 251 eV after in-situ cleaving the SRO$_{214}$ crystals at 10 K in ultra-high vacuum with base pressure lower than 5 x 10$^{-11}$ Torr.

Scanning Superconducting Quantum Interference Device (SQUID)
SQUID measurements are done using a custom-built piezoelectric-based scanning SQUID microscope with a 1 $\mu$m pick-up loop$^{49}$ and magnetic sensitivity of 1 $\mu$Φ$_0$ (Φ$_0 = 2.0678 \times 10^{-15}$ Tesla m$^2$ being the flux quantum). We use the scanning SQUID to image magnetic flux originating from the sample as a function of position. The magnetometry maps show the $z$ component of static magnetic flux near the surface of the sample. For the susceptometry measurements, we apply a local magnetic field of about 0.01-0.1 G using an on-chip field coil. Susceptometry is measured based on a standard lock-in technique and using the pick-up loop which resides at the centre of the field coil. An identical field coil surrounds a second pick-up loop used to correct for background magnetic fields in the magnetometry mode (gradiometric design).
Data availability

The datasets generated during and analysed during the current study are available from the corresponding authors on reasonable request. The raw muon data can be accessed using the data server with open access of the Paul Scherrer Institute (http://mususer.psi.ch/cgi-bin/SearchDB.cgi), where the same data sets can be also analyzed using the online software tools.

References

1. Maeno, Y. et al. Superconductivity in a layered perovskite without Copper. Nature 372, 532-534 (1994). https://doi.org/10.1038/372532a0
2. Illing, B. et al. Mermin-Wagner fluctuations in 2D amorphous solids. Proc. Natl. Acad. Sci. USA 114, 1856-1861 (2017). https://doi.org/10.1073/pnas.1612964114
3. Kosterlitz, J. M. & Thouless, D. J. Ordering, metastability and phase transitions in 2 dimensional systems. J. Phys. C Solid State Phys. 6, 1181-1203 (1973). https://doi.org/10.1088/0022-3719/6/7/010
4. Ji, D. et al. Freestanding crystalline oxide perovskites down to the monolayer limit. Nature 570, 87-90 (2019). https://doi.org/10.1038/s41586-019-1255-7
5. Bednorz, J. G. & Müller, K. A. Possible high Tc superconductivity in the Ba-La-Cu-O system. Z. Phys. B 64, 189-193 (1986). https://doi.org/10.1007/BF01303701
6. Imada, M., Fujimori, A. & Tokura, Y. Metal-insulator transitions. Rev. Mod. Phys. 70, 1039-1263 (1998). https://doi.org/10.1103/RevModPhys.70.1039
7. Cheong, S. W. & Mostovoy, M. Multiferroics: a magnetic twist for ferroelectricity. Nat. Mater. 6, 13-20 (2007). https://doi.org/10.1038/nmat1804
8. Luke, G. M. et al. Time-reversal symmetry-breaking superconductivity in Sr$_2$RuO$_4$. Nature 394, 558-561 (1998). https://doi.org/10.1038/29038
9. Xia, J., Maeno, Y., Beyersdorf, P. T., Fejer, M. M. & Kapitulnik, A. High resolution polar Kerr effect measurements of Sr$_2$RuO$_4$: evidence for broken time-reversal symmetry in the superconducting state. Phys. Rev. Lett. 97, 167002 (2006). https://doi.org/10.1103/PhysRevLett.97.167002
10. Pustogow, A. et al. Constraints on the superconducting order parameter in Sr$_2$RuO$_4$ from oxygen-17 nuclear magnetic resonance. Nature 574, 72-75 (2019). https://doi.org/10.1038/s41586-019-1596-2
11. Imai, T., Hunt, A. W., Thurber, K. R. & Chou, F. C. $^{17}$O NMR evidence for orbital dependent ferromagnetic correlations in Sr$_2$RuO$_4$. Phys. Rev. Lett. 81, 3006-3009 (1998). https://doi.org/10.1103/PhysRevLett.81.3006
12. Grinenko, V. et al. Split superconducting and time-reversal symmetry-breaking transitions, and magnetic order in Sr$_2$RuO$_4$ under uniaxial stress. Nat. Phys. 16, 789-794 (2020). https://doi.org/10.1038/s41567-020-0886-9
13. Matzdorf, R. et al. Ferromagnetism stabilised by lattice distortion at the surface of the $p$-wave superconductor Sr$_2$RuO$_4$. Science 289, 746-748 (2000). https://doi.org/10.1126/science.289.5480.746
14. Kirtley, J. R. et al. Upper limit on spontaneous supercurrents in Sr$_2$RuO$_4$. Phys. Rev. B 76, 014526 (2007). https://doi.org/10.1103/PhysRevB.76.014526
15. Damascelli, A. et al. Fermi surface, surface states and surface reconstruction in Sr$_2$RuO$_4$. Phys. Rev. Lett. 85, 5194-5197 (2000). https://doi.org/10.1103/PhysRevLett.85.5194
16. Shen, K. M. et al. Surface electronic structure of Sr$_2$RuO$_4$. Phys. Rev. B 64, 180502 (R) (2001). https://doi.org/10.1103/PhysRevB.64.180502
17. Di Bernardo, A. et al. Intrinsic paramagnetic Meissner effect due to s-wave odd-frequency superconductivity. Phys. Rev. X 5, 041021 (2015). https://doi.org/10.1103/PhysRevX.5.041021
18. Krieger, J. A. et al. Proximity-induced odd-frequency superconductivity in a topological insulator. Phys. Rev. Lett. 125, 026802 (2020). https://doi.org/10.1103/PhysRevLett.125.026802
19. Morenzoni, E. et al. Implantation studies of keV positive muons in thin metallic layers. Nucl. Instrum. Methods Phys. Res., Sect. B 192, 254-266 (2002). https://doi.org/10.1016/S0168-583X(01)01166-1
20. Suter, A. & Wojcik, B. M. Musrfit: a free platform-independent framework for μSR data analysis. Phys. Procedia 30, 69-73 (2012). https://doi.org/10.1016/j.phpro.2012.04.042
21. Luo, Y. et al. Normal state $^{17}$O NMR studies of Sr$_2$RuO$_4$ under uniaxial stress. Phys. Rev. X 9, 021044 (2019). https://doi.org/10.1103/PhysRevX.9.021044
22. Veenstra, C. N. et al. Determining the surface-to-bulk progression in the normal-state electronic structure of Sr$_n$RuO$_{4n+1}$ by angle-resolved photoemission and density functional theory. *Phys. Rev. Lett.* **110**, 097004 (2014). https://doi.org/10.1103/PhysRevLett.110.097004

23. Zabolotnyy, V. B. et al. Surface and bulk electronic structure of the unconventional superconductor Sr$_2$RuO$_3$: unusual splitting of the $\beta$ band, *New. J. Phys.* **14**, 063039 (2012). https://doi.org/10.1088/1367-2630/14/6/063039

24. Uemura, Y. J., Yamazaki, T., Harshman, D. R., Senba, M. & Ansaldo, E. J. Muon-spin relaxation in AuFe and Cu$_{n}$Mn spin glasses. *Phys. Rev. B* **31**, 546 (1985). https://doi.org/10.1103/PhysRevB.31.546

25. Chmaissem, O., Jorgensen, J. D., Shaked, H., Ikeda, S. & Maeno, Y. Thermal expansion and compressibility of Sr$_2$RuO$_3$. *Phys. Rev. B* **57**, 5067-5070 (1998). https://doi.org/10.1103/PhysRevB.57.5067

26. Boschker, H. et al. Ferromagnetism and conductivity in atomically thin SrRuO$_3$. *Phys Rev. X* **9**, 011027 (2019). https://doi.org/10.1103/PhysRevX.9.011027

27. Lago, J., Blundell, S. J., Eguia, A., Jansen, M. & Rojo, T. Three-dimensional Heisenberg spin-glass behavior in SrFe$_{0.94}$Co$_{0.10}$O$_{3.0}$. *Phys. Rev. B* **86**, 064412 (2012). https://doi.org/10.1103/PhysRevB.86.064412

28. Heffner, R. H. et al. Muon spin relaxation study of La$_{1-x}$Ca$_x$MnO$_3$. *Phys. Rev. B* **63**, 094408 (2001). https://doi.org/10.1103/PhysRevB.63.094408

29. Carlo, J. P. et al. New magnetic phase diagram of (Sr,Ca)$_2$RuO$_4$. *Nat. Mater.* **11**, 323-328 (2012). https://doi.org/10.1038/nmat3236

30. Chu, J. H., Kuo, H. H., Analytis, J. G. & Fisher, I. R. Divergent nematic susceptibility in an iron arsenide superconductor. *Science* **337**, 710-712 (2012). https://doi.org/10.1126/science.1221713

31. Wang, F., Kivelson, S. A. & Lee, D. H. Nematicity and quantum paramagnetism in FeSe. *Nat. Phys.* **11**, 959-963 (2015). https://doi.org/10.1038/nphys3456

32. Zhao, L. et al. Evidence of an odd-parity hidden order in a spin-orbit coupled correlated iridate. *Nat. Phys.* **12**, 32-36 (2016). https://doi.org/10.1038/nphys3517

33. Simon, M. E. & Varma, C. M. Detection and implications of a time-reversal breaking state in underdoped cuprates. *Phys. Rev. Lett.* **89**, 247003 (2002). https://doi.org/10.1103/PhysRevLett.89.247003

34. Scagnoli, V. et al. Observation of orbital currents in CuO. *Science* **332**, 696-698 (2011). https://doi.org/10.1126/science.1201061

35. Fischer, M. H. & Kim, E. A. Mean-field analysis of intra-unit-cell order in the Emery model of the CuO$_2$ plane. *Phys. Rev. B* **84**, 144502 (2011). https://doi.org/10.1103/PhysRevB.84.144502

36. Autieri, C., Cuoco, M. & Noce, C. Collective properties of eutectic ruthenates: Role of nanometric inclusions. *Phys. Rev. B* **85**, 075126 (2012). https://doi.org/10.1103/PhysRevB.85.075126

37. Mook, H. A., Sidis, Y., Fauqué, B., Balédent, V. & Bourges, P. Observation of magnetic order in a superconducting YBa$_2$Cu$_3$O$_{6.8}$ single crystal using spin polarized neutron scattering. *Phys. Rev. B* **78**, 020506 (R) (2008). https://doi.org/10.1103/PhysRevB.78.020506

38. Li, Y. et al. Unusual magnetic order in the pseudogap region of the superconductor HgBa$_2$CuO$_{4.6}$+$. Nature$ **455**, 372 (2008). https://doi.org/10.1038/nature07251

39. Fauqué, B. et al. Magnetic order in the pseudogap phase of high-$T_c$ superconductors. *Phys. Rev. Lett.* **96**, 197001 (2006). https://doi.org/10.1103/PhysRevLett.96.197001

40. Li, Z. Z., Wang, W. S. & Wang, Q. H. Competing orders in a three-orbital model of cuprates: is there a loop-current order? *Physica C Supercond.* **507**, 103 (2014). https://doi.org/10.1016/j.physc.2014.10.011

41. Klug, M., Kang, J., Fernandes, R. M. & Schmalian, J. Orbital loop currents in iron-based superconductors. *Phys. Rev. B* **97**, 155130 (2018). https://doi.org/10.1103/PhysRevB.97.155130

42. Bourges, P., Bounoua, D. & Sidis, Y. Loop currents in quantum matter. Preprint available at https://arxiv.org/pdf/2103.13295.pdf

43. Zhao, L. et al. Evidence of an odd-parity hidden order in a spin-orbit coupled correlated iridate. *Nat. Phys.* **12**, 32 (2016). https://doi.org/10.1038/nphys3517

44. Bounoua, D. et al. Loop currents in two-leg ladder cuprates. *Commun. Phys.* **3**, 123 (2020). https://doi.org/10.1038/s42005-020-0388-1

45. Malvestuto, M. et al. Electronic structure trends in the Sr$_{m+1}$Ru$_m$O$_{3n+1}$ family (n = 1,2,3). *Phys. Rev. B* **83**, 165121 (2011). https://doi.org/10.1103/PhysRevB.83.165121

46. Steppke, A. et al. Strong peak in $T_c$ of Sr$_2$RuO$_4$ under uniaxial pressure. *Science* **355**, eaaf9398 (2017). https://doi.org/10.1126/science.aaf9398
47. Willa, R., Hecker, M., Fernandes, R. M. & Schmalian, J. Inhomogeneous time-reversal symmetry breaking in \( \text{Sr}_2\text{RuO}_4 \). \textit{Phys. Rev. B} \textbf{104}, 024511 (2021). \url{https://doi.org/10.1103/PhysRevB.104.024511}

48. Shibata, A., Tanaka, H., Yonezawa, S., Nojima, T. & Maeno, Y. Quenched metastable vortex state in \( \text{Sr}_2\text{RuO}_4 \). \textit{Phys. Rev. B} \textbf{91}, 104514 (2015). \url{https://doi.org/10.1103/PhysRevB.91.104514}

49. Kirtley, J. R. et al. Scanning SQUID susceptometry of a paramagnetic superconductor. \textit{Phys. Rev. B} \textbf{85}, 224518 (2012). \url{https://doi.org/10.1103/PhysRevB.85.224518}

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Contributions
A.D.B. conceived the idea of the project and supervised it. The experiment was designed by A.D.B., Z.S. and A.V. The samples were grown by R.F. and A.V., and characterized by R.H., R.F., S. K., Y. Y., T. M., V. G. The LEED measurements were done by W. K. and C. K., and the SQUID measurements by A. B. and B. K. The muon measurements were performed by A.D.B., Z.S., R.H. with support from W. H., S. K., L. O. O., C. P. G., A. S., T. P., I. K. The muons results were analyzed by A.D.B., Z. S., M. C. with inputs from A. V., Y. M., E. S., J. R. and other authors. The theoretical model was developed by M. T. M. and M. C. with support from A. R. and C. N. The paper was written by A.D.B. with help from M. C. and Z. S. and inputs and comments from all the other authors.

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**Ethics declarations**

**Competing interests**
The authors declare no competing interests.