Unsplit superconducting and time reversal symmetry breaking transitions in Sr$_2$RuO$_4$
under hydrostatic pressure and disorder.

Vadim Grinenko,$^{1,2}$ Debarchan Das,$^3$ Ritu Gupta,$^3$ Bastian Zinkl,$^4$ Naoki Kikugawa,$^5$ Yoshiteru Maeno,$^6$ Clifford W. Hicks,$^{7,8}$ Hans-Henning Klaus,$^1$ Manfred Sigrist,$^4$ and Rustem Khasanov$^3$$^9$

$^1$Institute for Solid State and Materials Physics, Technische Universität Dresden, D-01069 Dresden, Germany
$^2$Leibniz-Institut für Festkörper- und Werkstoffforschung (IFW) Dresden, D-01171 Dresden, Germany
$^3$Laboratory for Muon Spin Spectroscopy, Paul Scherrer Institut, CH-5232 Villigen PSI, Switzerland
$^4$Institute for Theoretical Physics, ETH Zurich, CH-8093 Zurich, Switzerland
$^5$National Institute for Materials Science, Tsukuba 305-0003, Japan
$^6$Department of Physics, Kyoto University, Kyoto 606-8502, Japan
$^7$Max Planck Institute for Chemical Physics of Solids, D-01187 Dresden, Germany
$^8$School of Physics and Astronomy, University of Birmingham, Birmingham B15 2TT, United Kingdom

There is considerable evidence that the superconducting state of Sr$_2$RuO$_4$ breaks time reversal symmetry. In the experiments showing time reversal symmetry breaking its onset temperature, $T_{\text{TRSB}}$, is generally found to match the critical temperature, $T_c$, within resolution. In combination with evidence for even parity, this result has led to consideration of a $d_{xz} \pm id_{yz}$ order parameter. The degeneracy of the two components of this order parameter is protected by symmetry, yielding $T_{\text{TRSB}} = T_c$, but it has a hard-to-explain horizontal line node at $k = 0$. Therefore, $s \pm id$ and $d \pm ig$ order parameters are also under consideration. These avoid the horizontal line node, but require tuning to obtain $T_{\text{TRSB}} \approx T_c$. To obtain evidence distinguishing these two possible scenarios (of symmetry-protected versus accidental degeneracy), we employ zero-field muon spin rotation/relaxation to study pure Sr$_2$RuO$_4$ under hydrostatic pressure, and Sr$_{1.98}$La$_{0.02}$RuO$_4$ at zero pressure. Both hydrostatic pressure and La substitution alter $T_c$ without lifting the tetragonal lattice symmetry, so if the degeneracy is symmetry-protected $T_{\text{TRSB}}$ should track changes in $T_c$, while if it is accidental, these transition temperatures should generally separate. We observe $T_{\text{TRSB}}$ to track $T_c$, supporting the hypothesis of $d_{xz} \pm id_{yz}$ order.

INTRODUCTION

For unconventional superconductors identifying the symmetry of the order parameter is crucial to pinpoint the origin of the superconductivity. Unconventional pairing states are distinguished from conventional ones by a non-trivial intrinsic phase structure which causes additional spontaneous symmetry breaking at the superconducting phase transition. This can lead, for instance, to a reduction of the crystal symmetry or the loss of time reversal symmetry. Indeed, several superconductors are known, which show experimental responses consistent with time reversal symmetry breaking (TRSB) superconductivity [11][11].

TRSB superconducting states are formed by combining two or more order parameter components with complex coefficients. These components may be degenerate by symmetry, belonging to a single irreducible representation of the crystalline point group (as in the case of $p_x \pm ip_y$ or $d_{xz} \pm id_{yz}$ superconductivity on a tetragonal lattice), or they may originate from different representations (for example, $d_{xy} \pm id_{x^2-y^2}$ superconductivity on a tetragonal lattice). In the following, we refer to the former as single-representation and the latter as composite-representation order parameters. For composite-representation order parameters, the two components will generally onset at different temperatures. The higher transition temperature becomes $T_c$, the superconducting critical temperature, and the lower temperature $T_{\text{TRSB}}$, the temperature where time-reversal symmetry breaking onsets. The possibility of composite order parameters is usually dismissed out of hand, because it is unusual for two components that are not related by symmetry to be close enough in energy. However, there are a few known examples: $s$ and $d_{x^2-y^2}$ are relatively close in energy in iron-based superconductors [11][12], while both (U,Th)Be$_{13}$ [13][14] and UPt$_3$ [2][3][8] have split $T_c$ and $T_{\text{TRSB}}$.

Here, we study Sr$_2$RuO$_4$, an unconventional superconductor [13][14], in which the origin of the superconductivity remains a mystery. Evidence that this superconductor breaks time reversal symmetry comes from zero-field muon spin rotation/relaxation (ZF-$\mu$SR) experiments [15] and polar Kerr effect measurements [16]. Phase-sensitive probes using a corner SQUID device give further support [17]. Moreover, the Josephson effect between a conventional superconductor and Sr$_2$RuO$_4$ reveal features compatible with the presence of superconducting domains, as expected for TRSB superconductivity [18][20]. For two decades the leading candidate state to explain these and other observations was the chiral $p$-wave state $p_x \pm ip_y$ (the lattice symmetry of Sr$_2$RuO$_4$ is tetragonal), which has odd parity and therefore equal spin pairing. However, there is compelling evidence against an order parameter with such spin structure. This evidence includes paramagnetic limiting for in-plane magnetic fields [21][22] and the recently discovered drop in the NMR Knight shift below $T_c$ [24][25]. In combination with the above experimental support for TRSB superconductivity, this evidence compels consideration of $d_{xz} \pm id_{yz}$.
order.

d_{xz} \pm id_{yz} \approx 0$ order would be a surprise because it has a line node at $k_z = 0$, which under conventional understanding requires interlayer pairing, while in Sr$_2$RuO$_4$ interlayer coupling is very weak. It has been proposed that $d_{xz} \pm id_{yz}$ order might be obtained through multi-orbital degrees of freedom; in this model the order parameter symmetry is encoded in orbital degrees of freedom, so interlayer pairing is not required [24]. This form of pairing is also under consideration for URu$_2$Si$_2$ [27, 28]. However, so far it has not been unambiguously confirmed in any material. To avoid horizontal line nodes, the composite-representation order parameters $s \pm id_{x^2−y^2}$ [29], $s \pm id_{xy}$ [30] and $d_{x^2−y^2} \pm id_{y(x^2−y^2)}$ [31, 32] have also recently been proposed for Sr$_2$RuO$_4$. In contrast to $d_{xz} \pm id_{yz}$, these require tuning to obtain $T_c \approx T_{\text{TRSB}}$ on a tetragonal lattice.

In this work, to test whether the order parameter of Sr$_2$RuO$_4$ is of single- or composite-representation type we perform ZF-$\mu$SR measurements on hydrostatically pressured Sr$_2$RuO$_4$ and on La-doped Sr$_{2−y}$La$_y$RuO$_4$. Both of these perturbations maintain the tetragonal symmetry of the lattice. If the order parameter has single-representation nature, $T_{\text{TRSB}}$ will therefore track $T_c$. If the order parameter is of the composite-representation kind, with $T_{\text{TRSB}}$ matching $T_c$ in clean, unstressed samples through an accidental fine tuning, then perturbations away from this point should in general split $T_{\text{TRSB}}$ and $T_c$, whether they preserve tetragonal lattice symmetry or not [33]. Here, we have observed a clear suppression of $T_{\text{TRSB}}$ at a rate matching the suppression of $T_c$. Our experimental results provide evidence in favour of single-representation nature of the order parameter in Sr$_2$RuO$_4$.

FIG. 1: Setup for hydrostatic pressure experiments. (a) Sr$_2$RuO$_4$ sample, consisting of semi-cylindrical pieces glued on oxygen-free copper foils. The top and the bottom panels are the front and the side view, respectively. The crossed circle and the arrow indicate the orientation of the $c$-axis. (b) Construction of the pressure cell [34]. The sample and the pressure medium are surrounded only by beryllium-copper (the pressure cell body and the teflon cap support). The parts of the cell with strong $\mu$SR response (teflon cap and tungsten carbide piston) are far from the sample and outside of the muon beam. The initial muon spin polarization $P_\mu(0)$ and the external field $B_{\text{ext}}$ in TF-$\mu$SR measurements are aligned along the $x$- and $y$-axes, respectively. By rotating the cell about the $z$-axis, the angle between $P_\mu(0)$ and the sample $c$-axis can be varied.

EXPERIMENTAL DESIGN AND RESULTS

$\mu$SR on Sr$_2$RuO$_4$ under hydrostatic pressure

The hydrostatic pressure measurement setup is shown schematically in Fig. 1. Sr$_2$RuO$_4$ crystals of diameter $\varnothing \sim 3$ mm were affixed to oxygen-free copper foils, and assembled into an approximately cylindrical collection of total diameter $\varnothing \sim 7$ mm and total length $l \sim 12$ mm [see Fig. 1(a)]. The $c$-axes of the separate crystals were aligned to within 3°.

The pressure cell used in the present study [Refs. 34, 35 and Fig. 1(b)] is a modification of a classic $\mu$SR clamped pressure cell [35, 36]. It consists of a main body that encloses the sample and pressure medium, a teflon cap with a metallic support, a tungsten carbide piston, a pressing pad, and a clamping bolt (not shown) that holds the piston in place. All the metallic parts of the cell apart from the piston are made from a nonmagnetic beryllium-copper alloy, which is known to have a temperature-independent $\mu$SR response [34, 50]. The main feature of this cell is that the only materials placed in the muon beam are the sample, the pressure medium, and this CuBe alloy. The muons had a typical momentum of 97 MeV/c, sufficient to penetrate the walls of the pressure cell. The pressure medium was 7373 Daphne oil, which at room temperature solidifies at a pressure $p \approx 2.3$ GPa [37]. The maximum pressure reached here was 0.95 GPa, and therefore hydrostatic conditions are expected. The pressure was determined by monitoring the critical temperature of a small piece of indium (the pressure indicator) placed inside the cell with the Sr$_2$RuO$_4$ sample. Confirmation that essentially hydrostatic conditions were attained is provided by the fact that $T_c$ was observed to decrease linearly with pressure, whereas in-plane uniaxial stress on a GPa scale causes a strong non-linear increase in $T_c$ [38].

The samples used here were grown by the standard floating-zone method [40]. Measurements of heat capacity of pieces cut from the ends of the rods used here revealed an average $T_c$ of 1.30(6) K (see Fig. ED1 and the Methods section), slightly below the limit of $T_c$ of 1.50 K for a pure sample. $T_c$ and $T_{\text{TRSB}}$ were both obtained by means of $\mu$SR, ensuring that both quantities were measured for precisely the same sample volume. In the $\mu$SR method, spin-polarised muons are implanted, and their spins then precess in the local magnetic field. By collecting statistics...
of decay positrons in selected direction(s), the muon polarization as a function of time after implantation, \( P_\mu(t) \), can be determined; the time-evolution of this polarization is determined by the magnetic fields in the sample \[11\].

\( T_c \) is determined through transverse-field (TF) measurements. An external field \( B_{\text{ext}} \) of 3 mT was applied parallel to the crystalline c-axis and perpendicular to the initial muon spin polarization \( P_\mu(0) \). Measurements were performed in the field-cooled (FC) mode. Details of the method and analysis are given in the Methods section.

Example TF-\( \mu \)SR time spectra at pressure \( p = 0.95 \) GPa, and at a temperature above \( T_c \) and one below, are shown in Fig. 2(a). Above \( T_c \), the spins of muons stopped in both the sample and the pressure cell walls precess with frequency \( \omega = \gamma_\mu B_{\text{ext}} \) (where \( \gamma_\mu = 2\pi \times 135.5 \) MHz/T is the muon gyromagnetic ratio). The muon spin polarization is seen to relax substantially on a 10 \( \mu s \) time scale. This is because approximately 50\% of muons are implanted into the CuBe, where the nuclear magnetic moments of Cu rapidly relax their polarisation. Below \( T_c \), the internal field in the sample becomes highly inhomogeneous due to the appearance of a flux-line lattice, and so the polarisation of the muons that implanted in the sample also relaxes quickly.

TF-\( \mu \)SR measurements were performed at 0, 0.25, 0.62, and 0.95 GPa. Data at 0 and 0.95 GPa are shown in Fig. 2 and at the other two pressures in Figs. ED3 and ED4 in the Methods section. Data are analysed as a sum of background and sample contributions, given by Eqs. M2 and M3 (in the Methods section), respectively. From the sample contribution we extract a Gaussian relaxation rate, \( \sigma \), and the diamagnetic shift of the field inside the sample, \( B_{\text{int}} - B_{\text{ext}} \propto M_{\text{FC}} \) \[42\] (\( M_{\text{FC}} \) is the field-cooled magnetization). Figures 2(b) and (c) respectively show the temperature dependence of \( \sigma \) and \( B_{\text{int}} - B_{\text{ext}} \).

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section. The onset of superconductivity can be seen in both $\sigma$ and $B_{\text{int}} - B_{\text{ext}}$, as a transition rounded on a scale of approximately 0.1 K. The heat capacity measurements show a similar distribution of $T_c$'s; see Fig. ED1 and the Methods section.

The pressure dependence of $T_c$ is shown in Fig. 2(g). The error bars in the figure are the rounding on the transition, and can be taken as an absolute error on $T_c$. When fitting $\sigma(T)$ and $B_{\text{int}}(T)$ with model functions, the statistical error on the $T_c$'s extracted is considerably smaller, meaning that the error on changes in $T_c$ is low. A linear fit to $T_c(p)$ yields a slope $dT_c/dp = -0.24(2)$ K/GPa, which is in good agreement with literature data [44–46].

$\mu$SR on Sr$_1.98$La$_{0.02}$RuO$_4$

Substitution of La for Sr adds electrons to the Fermi surfaces; in Sr$_{2-y}$La$_y$RuO$_4$ this doping drives the largest Fermi surface through a Lifshitz transition from a hole-like geometry, at $y \approx 0.20$ [52–53]. At $y = 0.02$, the change in Fermi surface structure is minimal, and the main effect of the La substitution is to suppress $T_c$, through the added disorder. Heat capacity data, measured on a small piece cut from the $\mu$SR sample, give $T_c = 0.70(5)$ K, where the error reflects the width of the transition (see Fig. ED2).

This sample was studied at zero pressure. With no pressure cell material in the beam, the background is much smaller. The typical muon momentum was 28 MeV/c, giving of approximately 0.1 nm implantation depth [41]. Representative TF-$\mu$SR time spectra above and below $T_c$, where the applied field is $B_{\text{ext}} = 2$ mT parallel to the crystalline c-axis, are shown in Fig. 3(a). Below $T_c$, the muon spin polarisation relaxes almost completely on a 10 $\mu$s timescale, showing that essentially the entire sample volume is superconducting. The TF Gaussian relaxation rate $\sigma$ is shown in panel (b), and $B_{\text{int}} - B_{\text{ext}}$ in panel (c). These measurements yield $T_c = 0.75(5)$ K. The heat capacity data are also shown in panel (b).

ZF-$\mu$SR data are presented in Figs. 3(d) and (e). Fitting with Eq. 1 returns $\Delta \lambda = 0.007(1)$ $\mu$s$^{-1}$ and $T_{\text{TRSB}} = 0.8(1)$ K. This $\Delta \lambda$ is noticeably smaller than that obtained from the undoped Sr$_2$RuO$_4$, sample, corresponding to an internal field $B_{\text{TRSB}} \approx 0.01$ mT. It is, however, within the range of previous results [48]. In qualitative agreement with data on a lower-$T_c$ Sr$_2$RuO$_4$, reported in Ref. [47] though here with more data at $T > T_c$ to be certain of the base relaxation rate, this low value of $\Delta \lambda$ shows that $B_{\text{TRSB}}$ is not straightforwardly related to
FIG. 3: TRSB in Sr$_{1.98}$La$_{0.02}$RuO$_4$. (a) TF-$\mu$SR time-spectra above and below $T_c$ measured at $B_{\text{ext}} = 2$ mT with $B_{\text{ext}} \parallel c$. The solid lines are fits of Eq. 2 to the data. (b) and (c) Temperature dependencies of the Gaussian relaxation rate $\sigma$ and the diamagnetic shift $B_{\text{int}} - B_{\text{ext}}$, respectively. Arrows indicate the superconducting transition temperature $T_c$, determined from the TF-$\mu$SR data. The blue curve in panel (b) is the electronic specific heat $C_{el}/T$, measured on a small piece cut from the $\mu$SR sample. (d) ZF- and LF-$\mu$SR time-spectra. ZF data from above and below $T_c$, measured with $P_y(0) \parallel c$, are shown. The LF data are from $T$ well below $T_c$, and with $B_{\text{ext}} = 3$ mT $|| P_y(0)$. The solid lines are fits of Eq. 1 to ZF data. The blue curve is, again, $C_{el}/T$. Arrows indicates positions of $T_c$ and $T_{\text{TRSB}}$. (f) Double logarithmic plot of the normalized specific heat jump $\Delta C_{el}/\gamma_n T_{c}^{\text{SH}}$ versus $T_c^{\text{SH}}$ ($\gamma_n$ is the Sommerfeld coefficient and $T_{c}^{\text{SH}}$ is the transition temperature determined from $C_{el}/T(T)$ by means of equal-entropy construction, see Fig. ED1(a)). Filled symbols: data from this work; open symbols: data taken from Refs. [45, 46]. The displayed error bars for $\mu$SR data correspond to one standard deviation from the $\chi^2$ fit [39]. The error bars for $\Delta C_{el}/\gamma_n T_{c}^{\text{SH}}$ and $T_c^{\text{SH}}$ indicate uncertainty in selecting the temperature range for linear fit below $T_c$.

defect density. At present, the origin of the sample-to-sample variation in $B_{\text{TRSB}}$ is unknown.

Longitudinal-field (LF) measurements can be employed to determine whether internal fields are static or fluctuating. If $B_{\text{TRSB}}$ is static, under an applied field parallel to $P_y(0)$ that is considerably larger than $B_{\text{TRSB}}$, muon spin precession is greatly restricted and the spin polarisation does not relax (i.e. the muon spins decouple from $B_{\text{TRSB}}$). In contrast, fluctuating $B_{\text{TRSB}}$ can still relax the muon spin polarisation [11]. Data shown in panels (d) and (e) indicate that $B_{\text{ext}} || P_y(0) = 3$ mT fully suppresses the muon spin relaxation, and therefore that $B_{\text{TRSB}}$ is static on a microsecond time scale, in agreement with data on clean Sr$_2$RuO$_4$ reported in Ref. [13] We note that LF measurements were not performed on the hydrostatically pressurised sample because the decoupling field for the Cu background is of the order of 10 mT, considerably stronger than that for Sr$_2$RuO$_4$.

Heat capacity measurements

The specific heat measurements were performed at ambient pressure for several pieces of Sr$_{2-y}$La$_y$RuO$_4$ single crystals. The results are presented in Figs. 3(b) and (e) for Sr$_{1.98}$La$_{0.02}$RuO$_4$ ($y = 0.02$) and in the Methods section for Sr$_2$RuO$_4$ ($y = 0$, Fig. ED1), respectively. The specific heat jumps at $T_c$ ($\Delta C_{el}/\gamma_n T_{c}^{\text{SH}}$, $\gamma_n$ is the Sommerfeld coefficient) were further obtained in a way presented in Fig. ED2.

Figure 3(f) summarises the $\Delta C_{el}/\gamma_n T_{c}^{\text{SH}}$ vs. $T_c^{\text{SH}}$ data for our Sr$_{2-y}$La$_y$RuO$_4$ samples. Here $T_c^{\text{SH}}$ denotes the superconducting transition temperature determined from $C_{el}/T$ vs. $T$ measurement curves by means of equal-entropy construction algorithm, see Fig. ED1(a) and the Methods section. In addition, we have also included some literature data for Sr$_2$RuO$_4$ with different amount of disorder [45] and for Sr$_2$RuO$_4$ under uniaxial strain [46]. In total, Fig. 3(f) compares Sr$_2$RuO$_4$ samples with a factor of five variation in $T_c$. Remarkably, $\Delta C_{el}/\gamma_n T_{c}^{\text{SH}}$ vs. $T_c$ data points scale as $T_c^{\text{SH}}$ with $\alpha \approx 0.65$, which is dis-
It is worth noting here, that for most Fe-based superconductors, $\Delta C_{el}/\gamma n T_c$ follows approximately the BNC (Bud’ko-Ni-Canfield) scaling behavior $\Delta C_{el}/\gamma n T_c \propto T_c^\alpha$ with $\alpha \approx 2$ [54], which is considered to be a consequence of the unconventional multiband $s_{\pm}$ superconductivity. The change of the superconducting pairing state in the Ba$_{1-x}$K$_x$Fe$_2$As$_2$ system results in abrupt change of the scaling behavior leading to an intermediate $s + i s$ state [11].

**DISCUSSION**

In a previous ZF-$\mu$SR experiment, in-plane uniaxial pressure, which does lift the tetragonal symmetry of the unpressurised lattice, was found to induce a strong splitting between $T_c$ and $T_{TRSB}$ [48]. Uniaxial pressure drives a strong increase in $T_c$, while $T_{TRSB}$ varies much more weakly, probably decreasing slightly with initial application of pressure. The microscopic mechanism yielding the signal observed at $T_{TRSB}$, a weak enhancement in muon spin relaxation rate, remains unclear: the main proposed mechanism, magnetism induced at defects and domain walls by a TRSB superconducting order, is unproved experimentally [55, 56]. At present, the link between enhanced muon spin relaxation and TRSB superconductivity is, therefore, mainly empirical, based on: (i) the facts that it is a signal seen in only a small fraction of known superconductors, that it generally appears at $T_c$, and (ii) the general notion that TRSB superconductivity can in principle generate magnetic fields while muons detect magnetic fields. In Ref. [48] careful checks were performed to rule out instrumentation artefact as the origin of the signal at $T_{TRSB}$, and it was further argued that this signal is extremely difficult to obtain from a purely magnetic mechanism. Nevertheless, the weak observed variation of $T_{TRSB}$, while $T_c$ varied strongly, raised some doubt as to whether this signal is in fact associated with

![Graph showing the relation between $T_{TRSB}$ and $T_c$. The graph illustrates the dependence of the time reversal symmetry breaking temperature $T_{TRSB}$ on the superconductor transition temperature $T_c$. The closed symbols correspond to the results obtained in present studies under hydrostatic pressure up to 0.95 GPa in pure Sr$_2$RuO$_4$ (diamonds) and in the La doped Sr$_{2-y}$La$_y$RuO$_4$ with $T_c = 0.75(5)$ K (square). The open squares are the uniaxial pressure data for undoped Sr$_2$RuO$_4$ from Ref. [48]. The dashed line corresponds to $T_{TRSB} = T_c$. The minus signs at the pressure values denote the effect of 'compression' of the sample volume.](image-url)
the superconductivity.

Here, we have observed a clear suppression of $T_{\text{TRSB}}$ with hydrostatic stress, at a rate matching the suppression of $T_c$. This result further strengthens the evidence that enhanced muon spin relaxation is an indicator of TRSB superconductivity: $T_{\text{TRSB}}$ tracks $T_c$ when tetragonal lattice symmetry is preserved, while the splitting induced by uniaxial pressure shows unambiguously that it is a distinct transition, and not an artefact through some unidentified mechanism of the superconducting transition itself. Figure 4 shows $T_{\text{TRSB}}$ versus $T_c$. The data reported here, on hydrostatically pressurised Sr$_2$RuO$_4$ and on unpressurised Sr$_{1.98}$La$_{0.02}$RuO$_4$, fall on the $T_{\text{TRSB}} = T_c$ line, while the uniaxial pressure data from Ref. 48 clearly deviate from this line.

Our central finding that $T_{\text{TRSB}}$ tracks $T_c$ provides further support for the single-representation $d_{xz} \pm id_{yz}$ order parameter. Importantly, $d_{xz} \pm id_{yz}$ is the only spin-singlet order parameter consistent with the selection rules imposed by ultrasound and Kerr effect data. The sound velocity for longitudinal ultrasound modes is renormalized at a superconducting transition, generally. A jump at $T_c$ in ultrasound velocity for transverse modes, however, is a signature of a multi-component order parameter. Ultrasound data on Sr$_2$RuO$_4$ show precisely this type of renormalization [57, 58]. While these experimental results are not sensitive to the spin configuration, they impose other stringent conditions on the possible pairing symmetries [59, 60]. The polar Kerr effect mentioned above is a second experiment which provides symmetry-related constraints, being compatible only with chiral pairing states [16]. These two selection rules are obeyed by both the chiral $p$-wave and chiral $d$-wave state, though as noted in the Introduction, $p$-wave order appears to be ruled out by NMR Knight shift data [24, 25]. In contrast, the composite-representation states do not satisfy the requirements for both selection rules. The $d_{x^2-y^2} + id_{xy}$ states are constructed to be compatible with the ultrasound measurements, but they are not chiral [61, 61]. The $s + id_{x^2-y^2}$ state violates both selection rules [29]. It can be generally stated that any composite-representation pairing states in a tetragonal crystal, composed of components of two one-dimensional representations, would satisfy at most one of the two selection rules (see the Methods section).

Major challenges to $d_{xz} \pm id_{yz}$ order are the absence of a resolvable second heat capacity anomaly at $T_{\text{TRSB}}$ in measurements on uniaxially pressurised Sr$_2$RuO$_4$ [51], and, as already noted, the theoretical challenges in obtaining a horizontal line node in a highly two-dimensional metal [62]. We note in addition that an analysis of low-temperature thermal conductivity data indicated vertical, rather than horizontal, line nodes in Sr$_2$RuO$_4$. [63]. The theoretical objection to horizontal line nodes may be overcome through the complex nature of the multi-orbital band structure, including sizable spin-orbit coupling [64, 64, 65].

So we may conclude that our ZF-$\mu$SR data combined with the selection rules for ultrasound and polar Kerr effect and the NMR Knight shift behavior are consistent with the single-representation chiral $d_{xz} + id_{yz}$-wave state, while all composite-representation states suffer from several deficiencies. We note, however, that there are also empirical challenges to a hypothesis of $d_{xz} \pm id_{yz}$, and that the difficulty in reconciling apparently contradictory experimental results in Sr$_2$RuO$_4$ may mean that one or more major, apparently solid results will in time be found to be incorrect, either for a technical reason or in interpretation. Further experiments are therefore necessary.

METHODS

Sample preparation and characterisation

Sr$_{2-y}$La$_y$RuO$_4$ single crystals

Single crystals of Sr$_{2-y}$La$_y$RuO$_4$ were grown by means of a floating zone technique [40]. Samples for measurement under hydrostatic pressure (with $y = 0$), were cut from two rods, C140 and C171, that each grew along a (100) crystallographic direction. The rods have diameter $\varnothing \simeq 3$ mm. Two sections of length 8–12 mm were taken from each rod. These were then cleaved, forming semi-cylindrical samples with flat surfaces perpendicular to the c-axis.

The effect of La doping on the TRSB transition was studied on a single original Sr$_{2-y}$La$_y$RuO$_4$ crystal of length 8 mm. The La concentration was analyzed by an electron-probe micro-analysis and was found to be $y \simeq 0.02$. Before the $\mu$SR measurements, this rod was then cleaved into two semi-cylindrical pieces, again with the flat faces $\perp$ c.

Specific heat of Sr$_{2-y}$La$_y$RuO$_4$ at ambient pressure

Specific heat measurements were performed at zero pressure for several pieces of Sr$_{2-y}$La$_y$RuO$_4$ single crystals, cut from the rod used for $\mu$SR measurements.

For Sr$_2$RuO$_4$ used in hydrostatic pressure measurements, the electronic specific heat capacity $C_\text{el}/T$ was measured for four samples: one sample cut from each end of both the C140 and C171 sections. Results are presented in Fig. E1. The specific-heat critical temperature $T_c$ of each sample was obtained by an equal-entropy construction, illustrated in panel (a). The spread on the critical temperature of each sample is taken as $T_c^{\text{max}} - T_c^{\text{min}}$, where $T_c^{\text{max}}$ and $T_c^{\text{min}}$ are determined for each transition as illustrated in panel (b). $T_c$ was found to be 1.35(3) and 1.34(3) K for the two samples from rod C140, and 1.27(4) and 1.26(3) K for those from C171. Because both rods were used in the hydrostatic pressure measurements, we take a combined value
$T_c^{SH} = 1.30(6)$ K for the specific-heat critical temperature of these samples together.

FIG. ED1: Specific heat curves taken for four ending pieces of C140 and C171 Sr$_2$RuO$_4$ rods. The mean value of the ‘specific-heat’ superconducting transition temperature $T_c^{SH}$ is obtained by an equal-entropy construction of the idealized specific heat jump [panel (a)]. The minimum and maximum values of the transition temperature ($T_{c,min}$ and $T_{c,max}$) are determined from the crossing points of linearly extrapolated $C_{el}/T$ vs. $T$ curves in the vicinity of $T_c$ [panel (b)].

The temperature dependence of $C_{el}/T$ for a small piece cut from the Sr$_{1.98}$La$_{0.02}$RuO$_4$ µSR sample is presented in Figs. [3] (b) and (e). Figure ED2 show the same data, but with $C_{el}/T$ normalised by the Sommerfeld coefficient $\gamma_n$. The equal-entropy construction and estimates of $T_{c,min}$ and $T_{c,max}$ result in $T_c^{SH} = 0.70(5)$ K.

**µSR experiments**

The muon spin rotation/relaxation (µSR) experiments were performed at the µE1 and πE1 beamlines, using the GPD [35], and Dolly spectrometers (Paul Scherrer Institute, PSI Villigen, Switzerland). At the GPD instrument, experiments under pressure up to $p \approx 0.95$ GPa on undoped Sr$_2$RuO$_4$ were performed. At the Dolly spectrometer, measurements of Sr$_{1.98}$La$_{0.02}$RuO$_4$ at ambient pressure were conducted. At both instruments $^3$He cryostats equipped with the $^3$He insets (base temperature $T \approx 0.25$ K) were used.

At the GPD instrument, measurements in zero-field (ZF-µSR) and with the field applied transverse to the initial muon spin polarization $P_\mu(0)$ (TF-µSR) were performed. In two sets of ZF-µSR studies, $P_\mu(0)$ was set to be parallel to the $c$-axis and along the $ab$-plane, respectively. In TF-µSR measurements the small 3 mT magnetic field was applied parallel to the $c$-axis and perpendicular to $P_\mu(0)$.

At the Dolly instrument, in addition to ZF- and TF-µSR experiments, the longitudinal-field (LF) measurements were performed. In these studies 3 mT magnetic field was applied parallel to the $c$-axis and to the initial muon spin polarisation $P_\mu(0)$.

**µSR data analysis procedure**

The experimental data were analyzed by separating the µSR signal on the sample (s) and the background (bg) contributions [66]:

$$A_0 P(t) = A_s P_s(t) + A_{bg} P_{bg}(t).$$  \hspace{1cm} (M1)

Here $A_0$ is the initial asymmetry of the muon spin ensemble, and $A_s$ ($A_{bg}$) and $P_s(t)$ [$P_{bg}(t)$] are the asymmetry and the time evolution of the muon spin polarization for muons stopped inside the sample (outside of the sample), respectively.

In a case of µSR under pressure studies, the background contribution (approximately 50% of total µSR response) is determined by the muons stopped in the pressure cell body. At ambient pressure experiment the small background contribution (of the order of 5%) is caused by muons stopped in the sample holder and the cryostat windows.
TF-μSR

In TF-μSR experiments, the sample contribution was analyzed by using the following functional form:

\[ P_s^{\text{TF}}(t) = \exp \left[ -\frac{\sigma^2 t^2}{2} \right] \cos(\gamma \mu B_{\text{int}} t + \phi). \]  

(M2)

Here \( B_{\text{int}} \) is the internal field in the sample, \( \phi \) is the initial phase of the muon spin ensemble, and \( \gamma \mu \simeq 2\pi \times 135.5 \text{ MHz/T} \) is the muon gyromagnetic ratio. The Gaussian relaxation rate \( \sigma \) consists of the ‘superconducting’, \( \sigma_{sc} \), and nuclear moment, \( \sigma_{nn} \), contributions and it is defined as: \( \sigma^2 = \sigma_{sc}^2 + \sigma_{nn}^2 \). Here, \( \sigma_{sc} \) and \( \sigma_{nn} \) characterize the damping due to the formation of the flux-line lattice in the superconducting state and of the nuclear magnetic dipolar contribution, respectively. In the analysis, \( \sigma_{nn} \) was assumed to be constant over the entire temperature range and was fixed to the value obtained above \( T_c \), where only nuclear magnetic moments contribute to the muon depolarization rate [see Fig. ED3(a)].

The pressure cell contribution was described by using the following equation:

\[ P_{pc}^{\text{TF}}(t) = \exp \left[ -\frac{\sigma_{pc}^2 t^2}{2} \right] \cos(\gamma \mu B_{\text{ext}} t + \phi). \]  

(M3)

Here \( \sigma_{pc} \simeq 0.28 \ \mu s^{-1} \) is the field and the temperature independent relaxation rate of beryllium-copper [35], and \( B_{\text{ext}} \) is the externally applied field.

The solid lines in Fig. 2(a) correspond to the fit of TF-μSR data by using Eq. M1 with the sample and the background parts described by Eqs. M2 and M3. For the data presented in Fig. 3(a) the background contribution was described by non-relaxing function \( P_{\text{bg}}^{\text{TF}}(t) = \cos(\gamma \mu B_{\text{ext}} t + \phi) \). The good agreement between the fits and the data demonstrates that the above model describes the experimental data rather well.

With the external magnetic field applied along the crystallographic c-axis (\( B_{\text{ext}} \parallel c \)), the superconducting contribution into the Gaussian relaxation rate \( \sigma_{sc} \) becomes proportional to the inverse squared in-plane magnetic penetration depth \( \lambda_{ab} \) [34]. The proportionality coefficient between \( \sigma_{sc} \) and \( \lambda_{ab}^{-2} \) depends on the value of the applied field, the symmetry of the flux-line lattice and the angular dependence of the superconducting order parameter.

The temperature dependencies of the Gaussian relaxation rate \( \sigma \) and the diamagnetic shift \( B_{\text{int}} - B_{\text{ext}} \) are presented in Figs. 2(b), (c) and 3(b), (c) for \text{Sr}_2\text{RuO}_4\) and \text{Sr}_1.98\text{La}_{0.02}\text{RuO}_4\) samples, respectively.

ZF- and LF-μSR

The sample contribution includes both, the nuclear moment relaxation and an additional exponential relaxation \( \lambda \) caused by appearance of spontaneous magnetic fields [15]:

\[ P_{s}^{\text{ZF}}(t) = \text{GKT}_s(t) \ e^{-\lambda t}. \]  

(M4)

Here \( \text{GKT}(t) \) is the Gaussian Kubo-Toyabe (GKT) relaxation function describing the magnetic field distribution created by the nuclear magnetic moments [11, 17].

\[ \text{GKT}(t) = \frac{1}{3} + \frac{2}{3}(1 - \sigma_{GKT}^2 t^2) \ e^{-\sigma_{GKT}^2 t^2/2}. \]  

(M5)

\( \sigma_{GKT} \) is the GKT relaxation rate.

Muons implanted in beryllium-copper pressure cell body sense solely the magnetic field distribution created by copper nuclear magnetic moments and described as:

\[ P_{pc}^{\text{ZF}}(t) = \text{GKT}_{pc}(t) \]  

(M6)

with the temperature independent relaxation rate \( \sigma_{GKT,BeCu} \simeq 0.35 \ \mu s^{-1} \) [35].

Fits of Eq. M1 with the sample and pressure cell parts described by Eqs. M4 and M6 to the ZF-μSR data were performed globally. The ZF-μSR time-spectra taken at each particular muon spin polarization \( \{P_{\mu}(0)||ab \text{ and } P_{\mu}(0)||c\} \) and pressure \( (p = 0.0, 0.25, 0.62, \text{ and } 0.95 \ \text{GPa}) \) were fitted simultaneously with \( A_s, A_{pc}, \sigma_{GKT,\text{Sr}_2\text{RuO}_4}, \sigma_{GKT,\text{BeCu}}, \text{ and } \lambda_0 \) as common parameters, and \( \lambda \) as individual parameter for each particular data set. The solid green and purple lines in Figs. 2(d) correspond to the fit of ZF-μSR data by using Eq. M1 with the sample and the background parts described by Eqs. M4 and M6.

Note that the absence of strong nuclear magnetic moments in \text{Sr}_{2-p}\text{La}_p\text{RuO}_4\) leads to the corresponding Gaussian Kubo-Toyabe relaxation rate being nearly zero. Consequently, the analysis of ZF- and LF-μSR data for \text{Sr}_{1.98}\text{La}_{0.02}\text{RuO}_4\) was performed by using the simple-exponential decay function:

\[ P_{s}^{ZF,LF}(t) = e^{-\lambda t}. \]  

(M7)

The solid lines in Figs. 3(d) correspond to the fit of ZF-μSR data by using Eq. M1 with the sample part described by Eqs. M7 and the non-relaxing background \( P_{\text{bg}}^{ZF,LF}(t) = 1 \).

The temperature dependencies of the exponential relaxation rate \( \lambda \) are presented in Figs. 2(e,f) and 3(e) for \text{Sr}_2\text{RuO}_4\) and \text{Sr}_{1.98}\text{La}_{0.02}\text{RuO}_4\) samples, respectively.

ZF- and TF-μSR results at \( p = 0.25 \) and \( p = 0.62 \ \text{GPa} \)

FIGURES ED3 and ED4 show the results of TF- and ZF-μSR measurements on \text{Sr}_2\text{RuO}_4\) at \( p = 0.25 \) and 0.62 GPa. Arrows in panels (a) and (b) indicate the position of the superconducting transition temperature \( T_c \). Arrow in panel (c) indicate the TRSB transition temperature \( T_{\text{TRSB}} \).
FIG. ED3: (a) Temperature dependence of the Gaussian relaxation rate $\sigma$ measured at $p = 0.25$ GPa and the external field $B_{\text{ext}} = 3$ mT applied parallel to the crystallographic $c$-axis. (b) The diamagnetic shift of the internal field $B_{\text{int}} - B_{\text{ext}} \propto M_{\text{FC}}$ [22]. $M_{\text{FC}}$ is the field-cooled magnetization, at $p = 0.25$ GPa. Arrows in panels (a) and (b) indicate the position of the superconducting transition temperature $T_c$. (c) Temperature dependence of the ZF exponential relaxation rate $\lambda$ induced by spontaneous magnetic fields caused by TRSB effects at $p = 0.25$ GPa. The initial muon spin polarization $P_{\mu}(0)$ is parallel to the $ab$-plane. The solid line is the fit by means of Eq. (1) from the main text. Arrow indicate the position of TRSB transition temperature $T_{\text{TRSB}}$.

**Extraction of $T_c$ from the TF-$\mu$SR data**

The superconducting transition temperature $T_c$ was extracted from temperature dependencies of the Gaussian relaxation rate, $\sigma$, and the diamagnetic shift of the internal field, $B_{\text{int}} - B_{\text{ext}} \propto M_{\text{FC}}$, as they obtained in TF-$\mu$SR experiments [see Figs. 2(b,c), 3(b,c), ED3(a,b), and ED4(a,b)].

In a case of $\sigma(T)$ data, the transition temperature was defined as a crossing point of linearly extrapolated $\sigma(T)$ curve in the vicinity of $T_c$ with $\sigma = \sigma_{\text{nm}}$ line. Note that $\sigma_{\text{nm}}$ is constant over the entire temperature range and it corresponds to the value reached above $T_c$ [see Fig. ED3(a)].

From the diamagnetic shift data, the transition temperature was defined as a crossing point of linearly extrapolated $B_{\text{int}} - B_{\text{ext}}$ vs. $T$ curve in the vicinity of $T_c$ with $B_{\text{int}} - B_{\text{ext}} = 0$ line [see Fig. ED3(b)].

**Symmetry properties of the order parameters**

Several order parameters have been proposed for the time reversal symmetry-breaking superconducting state of Sr$_2$RuO$_4$. We would like here to give a brief overview on the different options and the symmetry requirements to satisfy the selection rules for two experiments: ultrasound velocity renormalization for the transverse $c_{66}$ mode and the polar Kerr effect. For tetragonal crystal symmetry with the point group $D_{4h}$ the even-parity spin-singlet pairing states can be listed according to the irreducible representations of $D_{4h}$, four one-dimensional ones $A_{1g}, A_{2g}, B_{1g}, B_{2g}$ and a two-dimensional one $E_u$. The pair wave function $\psi_T(k)$ of the corresponding states are given by

$\psi_{A_{1g}}(k) = \psi_0(k)$  \hspace{1cm} s-wave

$\psi_{A_{2g}}(k) = \psi_0(k)k_xk_y(k_x^2 - k_y^2)$  \hspace{1cm} $g_{xy}(x^2-y^2)$-wave

$\psi_{B_{1g}}(k) = \psi_0(k)k_x^2 - k_y^2$  \hspace{1cm} $d_{xz,xy}$-wave

$\psi_{B_{2g}}(k) = \psi_0(k)k_xk_y$  \hspace{1cm} $d_{xy}$-wave

$\psi_{E_u}(k) = \{\psi_0(k)k_xk_z, \psi_0(k)k_yk_z\}$ \hspace{1cm} $\{d_{xz,dyz}\}$-wave (M8)
where \( \psi_0(\mathbf{k}) \) is a function of \( \mathbf{k} \) invariant under all symmetry operations of the tetragonal lattice. We list here first the composite-representation TRSB states:

\[
\begin{align*}
\tilde{\Gamma}_1 &= A_{1g} \otimes A_{2g} : s + i g \text{-wave} \\
\tilde{\Gamma}_2 &= A_{1g} \otimes B_{1g} : s + i d \text{-wave} \\
\tilde{\Gamma}_3 &= A_{1g} \otimes B_{2g} : s + i d' \text{-wave} \\
\tilde{\Gamma}_4 &= B_{1g} \otimes A_{2g} : d + i g \text{-wave} \\
\tilde{\Gamma}_5 &= B_{2g} \otimes A_{2g} : d' + i g \text{-wave} \\
\tilde{\Gamma}_6 &= B_{1g} \otimes B_{2g} : d + i d' \text{-wave}
\end{align*}
\]

Note that in general different representations correspond to different critical temperature. Thus to obtain a single superconducting phase transition for the composite states an accidental degeneracy of two representations is necessary. The two states proposed so far are \( \tilde{\Gamma}_2 \) \([29,30]\) and \( \tilde{\Gamma}_4 \) \([31,32]\). The two-dimensional representation allows for the combination

\[
\tilde{\Gamma}_7 = E_g : \text{chiral } d\text{-wave}
\]

with a pair wave function \( \psi_{E_g}(\mathbf{k}) = \psi_0(\mathbf{k})k_z(k_x \pm ik_y) \) as proposed in Refs. \([29,32]\). All composite states, \( \tilde{\Gamma}_{1-6} \), can be constructed by electron pairing within the RuO\(_2\) planes, while the state \( \tilde{\Gamma}_7 \) requires interlayer pairing. Due to the spin singlet nature all states are compatible with the new NMR Knight shift results \([24,25]\). All TRSB state are expected to generate internal spontaneous cur-

Turning to the odd-parity states the analogous picture arises with

\[
\begin{align*}
d_{A_{1u}}(\mathbf{k}) &= \psi_0(\mathbf{k})(\hat{x}k_x + \hat{y}k_y) \\
d_{A_{2u}}(\mathbf{k}) &= \psi_0(\mathbf{k})(\hat{x}k_y - \hat{y}k_x) \\
d_{B_{1u}}(\mathbf{k}) &= \psi_0(\mathbf{k})(\hat{x}k_x - \hat{y}k_y) \\
d_{B_{2u}}(\mathbf{k}) &= \psi_0(\mathbf{k})(\hat{x}k_y + \hat{y}k_x) \\
d_{E_v}(\mathbf{k}) &= \psi_0(\mathbf{k})(\hat{z}k_x, \hat{z}k_y)
\end{align*}
\]

\( d_{E_v}(\mathbf{k}) \) here listed in the convenient \( d \)-vector notation for spin-triplet pairing states (see \([68]\)). It is important to note that all composite phases from combination of two pairing states of one-dimensional representation are \( c \)-axis equal spin state and would be in agreement with present time NMR Knight data \([24,25]\) and had been proposed as possible states in Refs. \([69,70]\). These states are also called helical state in literature, as they are topologically non-trivial with helical surface states. The Knight shift experiments disagree with expectations of the state in representation \( E_v \) which yields the chiral \( p \)-wave state.

Again we have to make composite states of the one-dimensional representation to obtain TRSB phases. Analogous to the even-parity case we do not find any composite state which satisfies both selection rules, in contrast to the chiral \( p \)-wave state which behaves the same way as the chiral \( d \)-wave state in this respect.

**DATA AVAILABILITY**

The data represented in Figs. 2 – 4 are available as Source Data. All other data that support the plots within this paper and other findings of this study are available from the corresponding author upon reasonable request.

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**AUTHOR INFORMATION**

**Author contributions**

R.K, V.G, and M.S conceived the project. Data were taken by R.K, V.G. D.D, and R.G. R.K and V.G performed data analysis and interpreted the results together with M.S.. B.Z and M.S. provided the theoretical analysis. N.K. provided and characterized samples. R.K, V.G., M.S., and C.W.H. wrote the manuscript with inputs from all authors.

**Corresponding Authors**

Correspondence to Vadim Grinenko or Manfred Sigrist or Rustem Khasanov.

**ETHICS DECLARATIONS**

**Competing interests**

The authors declare no competing interests.

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* Electronic address: v.grinenko@ifw-dresden.de
† Electronic address: mansigri@ethz.ch
‡ Electronic address: rustem.khasanov@psi.ch

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