Constraints on the superconducting order parameter in Sr_2RuO_4 from ^{17}O NMR

A. Pustogow[1*], Yongkang Luo[1,2*], A. Chronister[1], Y.-S. Su[1], D. A. Sokolov[3], F. Jerzembeck[3], A. P. Mackenzie[3,4], C. W. Hicks[3], N. Kikugawa[5], S. Raghu[6], E. D. Bauer[7], and S. E. Brown[1]

[1]*Department of Physics & Astronomy, UCLA, Los Angeles, CA 90095, USA;*

[2]*Wuhan National High Magnetic Field Center and School of Physics, Huazhong University of Science and Technology, Wuhan 430074, China;*

[3]*Max Planck Institute for Chemical Physics of Solids, Dresden 01187, Germany;*

[4]*Scottish Universities Physics Alliance, School of Physics and Astronomy, University of St Andrews, St Andrews KY16 9SS, UK;*

[5]*National Institute for Materials Science, Tsukuba 305-0003, Japan;*

[6]*Geballe Laboratory for Advanced Materials, Stanford University, Stanford, CA, 94305, USA;*

[7]*Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA.*

Phases of matter are usually identified through the lens of spontaneous symmetry breaking, which particularly applies to unconventional superconductivity and the interactions it originates from. In that context, the superconducting state of the quasi-two-dimensional and strongly correlated Sr_2RuO_4 is uniquely held up as a solid-state analog to superfluid ^{3}He-*A*[1,2], with an odd-parity vector order parameter that is unidirectional in spin space for all electron momenta and also breaks time-reversal symmetry. This characterization was recently

---

[*] These authors contributed equally to this work.

called into question by a search for, and failure to find, evidence for an expected "split" transition while subjecting a $\mathrm{Sr_2RuO_4}$ crystal to in-plane uniaxial pressure; instead a dramatic rise and peak in a single transition temperature was observed [3,4]. NMR spectroscopy, which is directly sensitive to the order parameter via the hyperfine coupling to the electronic spin degrees of freedom, is exploited here to probe the nature of superconductivity in $\mathrm{Sr_2RuO_4}$ and its evolution under strained conditions. A reduction of Knight shifts K is observed for all strain values and temperatures $T < T_c$, consistent with a drop in spin polarization in the superconducting state. In unstrained samples, our results are in contradiction with a body of previous NMR work [5], and with the most prominent previous proposals for the order parameter. $\mathrm{Sr_2RuO_4}$ is an extremely clean layered perovskite, and the superconductivity emerges from a strongly correlated Fermi Liquid. The present work imposes tight constraints on the order-parameter symmetry of this archetypal system.

The normal state of $\mathrm{Sr_2RuO_4}$ is based on three bands crossing the Fermi level [6,7], with pronounced strong-correlation characteristics linked to Hund's Rule coupling of the partially filled Ru t_{2g} orbitals dominating the Fermi surface. The transition to a superconducting ground state at $T_c = 1.5$ K [8], with indirect evidence for proximity to ferromagnetism, led to the suggestion that the pair wave functions of the superconducting state likely exhibit a symmetric spin part, *i.e.*, triplet [1]. Crucial support for the existence of a triplet order parameter rested on NMR spectroscopy, which showed no change in Knight shift between normal and superconducting states[5]. Later, several experiments produced evidence for time-reversal symmetry breaking (TRSB) [9,10]. Together, these reports aligned well to the above-mentioned proposal that $\mathrm{Sr_2RuO_4}$ is a very clean, quasi two-dimensional solid-state analog of the topologically nontrivial ^{3}He-A phase [11], but here in the form of a charged superfluid.

However, several experimental results are difficult to reconcile with the proposed p-wave superconducting state [12–14]. For instance, due to TRSB, there is the generic expectation of measurable chiral edge currents (which propagate within a coherence length of the edge, but which are screened over a somewhat larger penetration depth scale). However, such currents have not been detected despite several attempts with progressively improved sensitivity [15–17].

In mean-field theory, a chiral p-wave superconductor subjected to in-plane uniaxial strain ε_{aa} exhibits a split transition, and accompanying cusp about $\varepsilon_{aa} = 0$. However, strained samples of Sr_2RuO_4 exhibit neither; observed instead is a large increase in T_c $(1.5 \rightarrow 3.5$ K), that peaks at $\varepsilon_{aa} = \varepsilon_v \equiv -0.5\%$ [4]. The behavior was interpreted as a consequence of tuning the Fermi energy E_F of the quasi-2D band through a van Hove singularity (vHs), and concomitant singularity in the density of states (DOS) at E_F [18]. These observations motivated a study of ^{17}O nuclear magnetic resonance (NMR) in uniaxially pressurized samples; indeed, evidence for the DOS maximum and accompanying enhanced Stoner factor came from normal-state ^{17}O NMR experiments [19]. The results have bearing on the chiral p-wave state hypothesis: on the one hand, an odd-parity order parameter vanishes at the location of the vHs, thereby reducing the impact of the DOS enhancement; on the other hand, the enhanced Stoner factor and ferromagnetic fluctuations could strengthen the pairing instability.

The focus of this paper is ^{17}O NMR Knight shift studies on uniaxially pressurized Sr_2RuO_4, comparing the shifts seen in the normal and superconducting states. The experiments were carried out in a variable-strain device [20,21], and cover the full range of T_c from 1.5 K to 3.5 K. ^{17}O NMR spectroscopy is directly sensitive to the spin polarization M_s; the expectation for an s-wave (singlet) superconductor is a reduction in the paramagnetic shift, which would vanish in the limit $T/T_c \to 0$ and $B/B_{c2} \to 0$, whereas for the widely proposed E$_u$ state (Table 1) $K_s \equiv M_s(B)/B$ [22] remains unchanged from the normal-state value. Summarizing the findings, onset of superconductivity leads to a substantial drop in M_s for all strains measured; the zero-strain results are therefore in disagreement with those previously reported [5]. We describe a series of tests which, we believe, account for this discrepancy. While M_s remains nonzero for $T \to 0$, note that quasiparticle creation occurs for several possible reasons in applied fields $B_0 \neq 0$. No evidence for a change in ground state symmetry is observed as the strain is varied over the interval $\varepsilon_{aa} = [0, \varepsilon_v]$.

The crystal structure of Sr$_2$RuO$_4$ is identical to that of the undoped parent compound of the "214" cuprates, La$_2$CuO$_4$. Likewise, the states at E_F are predominantly of d character; here they derive from Ru t_{2g}-O π hybridization. Extended Data Fig. 1a depicts the orbitals dominating the γ band, associated with the Ru, O(1), O(1$'$) sites. The O(2) sites are in the apical positions, symmetrically above and below the Ru site. Throughout this report, the magnetic field $\mathbf{B_0} \parallel \mathbf{b}$, since out-of-plane field components suppress B_{c2}. On stressing the sample, the relevant response is the resulting asymmetric strain $\varepsilon_{aa} - \varepsilon_{bb}$; only ε_{aa} is noted here.

Since magnetic fields lead to quasiparticle spin polarization, the ideal experiment has the applied field $B_0 \ll B_{c2}$. Nuclear spin polarization, on the other hand, favors the largest field possible. For guidance in making this compromise in the choice of experimental parameters, we determined $B_{c2}(\varepsilon_{aa})$ (see Methods) and present the results in Fig. 1. B_{c2} is maximized at ε_v, coincident with T_c^{max}, at a value (4.3 ± 0.05 T) within a few per cent of that (4.5 T) reported in Ref. [4]. The reduction could be a result of a small misalignment from the in-plane condition, $O(1°)$ [14,23]. The minimum value is $B_{c2}(\varepsilon_{aa}) = 1.32 \pm 0.05\mathrm{T}$, identified by extending the measurements to tensile strains $\varepsilon_{aa} > 0$.

The temperature dependences of the ^{17}O central transition frequencies for the three sites were measured at $\varepsilon_{aa} = \varepsilon_v$, where B_{c2} is largest, at B_0=1.9980 T. The resulting spectra, shown in Fig. 2, reveal pronounced changes in shift upon decreasing the temperature through $T_c(B_0)$. Since the orbital shifts are relatively small, the frequencies corresponding to $K = 0$ (vertical dashed lines) are attributed to quadrupolar effects [19].

Since the normal-state Knight shifts $K_{1b} < 0$, $K_{1'b} > 0$, the changes for $T < T_c$ in Fig. 2b correspond to a drop in M_s of order 20–30 %, qualitatively different from the zero-strain results [5]. Note that the shifts $K \sim M_s/B_0$, remain nonzero for $T \rightarrow 0$, where field-induced quasiparticles are likely relevant at the relatively high fields ($B_0/B_{c2} \simeq 0.45$) at which the measurement was performed. In addition to the contributions from vortex cores, two other sources should be considered in the context of gap nodes, or at least the deep minima; these are the Volovik Effect [24], and Zeeman coupling.

The observed drop of M_s upon entering the superconducting state under strained conditions invites a comparison to the previous zero-strain experiments, for which the lack of reported decrease constituted a cornerstone of the case for a chiral p-wave order parameter. Therefore, we carried out measurements covering the entire interval $\varepsilon_{aa} = [0, \varepsilon_v]$. In doing so, the results were found to depend on NMR pulsing details. With this important observation in mind, a reexamination of the shifts for $\varepsilon_{aa} = 0$ is presented first.

In Fig. 3 we present the spectra with no applied stress, collected following various pulse excitations. The applied field is $B_0 = 0.7107$ T, similar to the 0.65 T used in Ref. [5], and the mixing chamber temperature is $T_{MC} = 20$ mK. Note that from Fig. 1, $B_0/B_{c2}(\varepsilon_{aa} = 0) \simeq 0.55$. As above, the three spectral lines shown are the central transitions for O(1), O(2) and O(1′), from low to high frequency, respectively. The top trace of Fig. 3a corresponds to the normal state at $T = 1.8$ K, collected using a standard two-pulse echo pulse sequence, $[\pi/2 - t_1 - \pi - acquire]$. The remaining spectra are all recorded at 20 mK base temperature, and transformed from transients following single-pulse excitations of variable time durations d_1, chosen because it is far less constraining than the echo sequence in regard to the amount of energy transmitted. These are ordered bottom-to-top with increasing pulse energy. Fig.3b depicts the shifts *vs.* pulse energy E; the variations are approximately linear for smaller energies, and saturate near to the normal-state values for higher energies.

It is tempting to assign the evolution, K *vs.* E, to "instantaneous" sample heating, such that the spectra are recorded while $T > T_c(B_0)$. Indeed, eddy currents resulting from the high amplitude RF pulses provide a mechanism for absorption. Moreover, the heat capacity vanishes continuously in the limit $T \to 0$. Consequently, a larger temperature increase results from a given amount of energy dissipated at lower temperatures. Note that a check of the nuclear spin-lattice relaxation time T_1 is usually insensitive to such an effect, since the time scales for T_1 and electronic thermal relaxation are so different, $T_1 >> \tau_{th}$. Therefore, it is possible that the spectra recorded following high-energy pulses correspond to those of the normal state, while T_1 results correspond to the superconducting state. For insight into the thermal conditions imposed by the RF pulses, time-synchronous measurements of the tank circuit reflected power were carried out. A summary of the conditions is as follows: an RF pulse (or sequence), as used for the NMR excitation, "pumps" the system. It is followed by a low-power RF probe, and the reflection is phase-sensitively detected using the NMR receiver. In this way we study the temporal changes to the reflected power, which depends on the sample response to the RF. Note that this is equivalent to an ac susceptibility measurement, and relates to RF shielding. Comparisons to the normal state are possible by measuring also the field dependence, including $B_0 > B_{c2}$, or by warming to $T > T_c(B_0 = 0)$.

Our results for in-phase (IP) and quadrature (Q) components of the reflected power are shown in Fig. 4, where the applied pulse energies cover the range used for the NMR measurements. Note that the overall phase is arbitrary. For sufficiently high energy pulses, the recovery to a steady state takes place via a two-step process. Aided by comparing to similar measurements carried out in varying fields (see Methods, Extended Data Fig. 5), our interpretation is that the sample under study is initially responding as though it is in the normal state. This lasts for a period of about 100 μs. A second, longer period of relaxation (O(1 ms)), occurs within the superconducting state. The longer time is likely due to changing vortex structure, motion and creep. No such time dependence is observed if the sample is initially in the normal state.

In summarizing the results presented so far, the experiments indicate a reduced spin polarization upon entering the superconducting state at zero strain, as well as at ε_v. The field strengths relative to the upper critical field were $B_0/B_{c2} = 0.55$ and 0.45, respectively. An important question is whether there is any indication for a change in order parameter symmetry between these limiting cases. Toward that end, spectra from normal and superconducting states were recorded for strains covering the interval $\varepsilon_{aa} = [0, \varepsilon_v]$ (see Extended Data Fig. 5 and Methods). Collected at fields 0.7107 T, 1.1573 T, the data in the superconducting state vary continuously, with no discernible jump in M_s. Since one route to a symmetry change is via a first-order phase transition, these results, when combined with the smooth variations of B_{c2} (Fig. 1) and the previously measured T_c[4], suggest this possibility unlikely.

The key experimental finding reported here is our deduction that, at all applied uniaxial pressures, the spin susceptibility deduced from our Knight shift measurements is substantially suppressed at 20 mK from the normal-state value. For unstrained samples, this result is therefore inconsistent with the previously considered $\mathbf{d} = \hat{\mathbf{z}}(k_x \pm ik_y)$ order parameter, or indeed any odd-parity state with an out-of-plane $\mathbf{d}$. Since such order parameters have been widely postulated to be relevant to Sr_2RuO_4 for over twenty years, this represents a major advance in our understanding of this exemplar of unconventional superconductivity.

Although we can rule out specific odd-parity order parameters of the type described above, we cannot rule out all odd-parity states on the basis of our NMR data alone. In Table 1, we present a broader summary of the expected Knight-shift changes for symmetry-allowed order parameters in $\mathrm{Sr_2RuO_4}$; a partial drop of the spin susceptibility is predicted in some cases. The magnitude of the drop that we see is therefore important. The uncertainty in estimating the quasiparticle background signal at $B_0/B_{c2} \sim 0.5$ also means that we cannot definitively distinguish odd-parity order parameters with in-plane $\mathbf{d}$-vectors (such as the $\mathrm{A}_{1,2u}$ and $\mathrm{B}_{1,2u}$ states in Table 1) from even parity states at all measured strains. By reducing the measurement field to 0.7107 T, we obtain a drop of 75% in the Knight shift at $\varepsilon_{aa} = \varepsilon_v$, see Extended Data Fig. 5. If that is all attributable to the spin susceptibility it would indeed rule out all the triplet states listed in Table 1. For the unstrained samples we observe a maximum Knight-shift reduction of approximately 50%, not inconsistent with $\mathrm{A}_{1,2u}$ or $\mathrm{B}_{1,2u}$ symmetry. We believe that further work on larger and more completely ^{17}O enriched samples will enable determination of whether the true reduction is more than 50% in the unstrained case. We note that reconciling with the independent observations of TRSB would require some amount of fine-tuning or some unusual physics. For instance, one may consider a situation in which, accidentally, the A_{1u} and B_{1u} states had nearly identical transition temperatures. In that case, one may imagine forming distinct domains, some stabilizing the A_{1u} state, others the B_{1u} state, and with non-trivial relative phases between such domains resulting in TRSB. Since NMR is a local probe, domains of this kind would generally produce distinct line shapes which we do not observe. In the even-parity sector, the tetragonal crystal field prevents in-plane paired states such as $d_{x^2-y^2}$ and d_{xy} from having the same T_c, so the only plausible TRSB order parameter would be of the form $d_{xz} \pm i d_{yz}$ (ψ_{chiral} in Table 1), an exotic state for which the Cooper pairing would be between electrons in adjacent planes. For any bulk TRSB state, however, transition splitting under uniaxial pressure is expected. Since a split transition has not yet been observed, either in our work or elsewhere [25], extending TRSB-sensitive measurements to strained Sr_2RuO_4 is a priority for future work. Overall, these are exciting times for research on Sr_2RuO_4, with the promise of a fundamentally new framework with which to understand its enigmatic superconductivity.

References

1. Rice, T. M. & Sigrist, M. Sr_2RuO_4: an electronic analogue of ^{3}He? J. Phys. : Condens. Matter **7**, L643–L648 (1995).
2. Mackenzie, A. P. & Maeno, Y. The superconductivity of Sr_2RuO_4 and the physics of spin-triplet pairing. Rev. Mod. Phys. **75**, 657–712 (2003).
3. Hicks, C. W. et al. Strong Increase of T_c of Sr_2RuO_4 Under Both Tensile and Compressive Strain. Science **344**, 283–285 (2014).
4. Steppke, A. et al. Strong peak in T_c of Sr_2RuO_4 under uniaxial pressure. Science **355**, eaaf9398 (2017).
5. Ishida, K. et al. Spin-triplet superconductivity in Sr_2RuO_4 identified by ^{17}O Knight shift. Nature **369**, 658–660 (1998).
6. Oguchi, T. Electronic band structure of the superconductor Sr_2RuO_4. Phys. Rev. B **51**, 1385–1388 (1995).

7. Mackenzie, A. P. et al. Quantum Oscillations in the Layered Perovskite Superconductor Sr_2RuO_4. Phys. Rev. Lett. **76**, 3786–3789 (1996).

8. Maeno, Y. et al. Superconductivity in a layered perovskite without copper. Nature **372**, 532–534 (1994).

9. Luke, G. M. et al. Time-reversal symmetry-breaking superconductivity in Sr_2RuO_4. Nature **394**, 558–561 (1998).

10. Xia, J., Maeno, Y., Beyersdorf, P. T., Fejer, M. M. & Kapitulnik, A. High Resolution Polar Kerr Effect Measurements of Sr_2RuO_4: Evidence for Broken Time-Reversal Symmetry in the Superconducting State. Phys. Rev. Lett. **97**, 167002 (2006).

11. Leggett, A. J. A theoretical description of the new phases of liquid ^3He. Rev. Mod. Phys. **47**, 331–414 (1975).

12. Yonezawa, S., Kajikawa, T. & Maeno, Y. First-Order Superconducting Transition of $\mathrm{Sr_2RuO_4}$. Phys. Rev. Lett. **110**, 077003 (2013). URL `https://link.aps.org/doi/10.1103/PhysRevLett.110.077003`.

13. Hassinger, E. et al. Vertical Line Nodes in the Superconducting Gap Structure of Sr_2RuO_4. Phys. Rev. X **7**, 011032 (2017).

14. Kittaka, S. et al. Searching for Gap Zeros in Sr_2RuO_4 via Field-Angle-Dependent Specific-Heat Measurement. J. Phys. Soc. Jpn. **87**, 093703 (2018).

15. Björnsson, P. G., Maeno, Y., Huber, M. E. & Moler, K. A. Scanning magnetic imaging Sr_2RuO_4. Phys. Rev. B **72**, 012504 (2005).

16. Hicks, C. W. et al. Limits on superconductivity-related magnetization in Sr_2RuO_4 and $PrOs_4Sb_{12}$ from scanning SQUID microscopy. Phys. Rev. B **81**, 214501 (2010).

17. Watson, C. A., Gibbs, A. S., Mackenzie, A. P., Hicks, C. W. & Moler, K. A. Micron-scale measurements of low anisotropic strain response of local T_c in Sr_2RuO_4. Phys. Rev. B **98**, 094521 (2018).

18. Sunko, V. et al. Direct Observation of a Uniaxial Stress-driven Lifshitz Transition in Sr_2RuO_4 (2019). URL `http://arxiv.org/abs/1903.09581`. `1903.09581`.

19. Luo, Y. et al. Normal State ^{17}O NMR Studies of Sr_2RuO_4 under Uniaxial Stress. Phys. Rev. X **9**, 021044 (2019). URL `https://link.aps.org/doi/10.1103/PhysRevX.9.021044`.

20. Hicks, C. W., Barber, M. E., Edkins, S. D., Brodsky, D. O. & Mackenzie, A. P. Piezoelectric-based apparatus for strain tuning. Rev. Sci. Instrum. **85**, 065003 (2014).

21. URL `https://razorbillinstruments.com/uniaxial-strain-cell/`.

22. Usually written as the product of a hyperfine coupling and spin susceptibility, this more general definition allows for nonlinear response.

23. Kittaka, S. et al. Angular dependence of the upper critical field of Sr_2RuO_4. Phys. Rev. B **80**, 174514 (2009).

24. Volovik, G. E. Superconductivity with lines of GAP nodes: density of states in the vortex. JETP Lett. **58**, 469–473 (1993).

25. Li, Y. S. et al. High precision heat capacity measurements on Sr_2RuO_4 under uniaxial pressure (2019). URL `http://arxiv.org/abs/1906.07597`. `1906.07597`.

26. Vollhardt, D. & Woelfle, P. The Superfluid Phases Of Helium 3 (CRC Press, 1990).

27. Matano, K., Kriener, M., Segawa, K., Ando, Y. & Qing Zheng, G. Spin-rotation symmetry breaking in the superconducting state of $Cu_xBi_2Se_3$. Nat. Phys. **12**, 852–854 (2016).

28. Veenstra, C. N. et al. Spin-orbital entanglement and the breakdown of singlets and triplets in Sr_2RuO_4 revealed by spin- and angle-resolved photoemission spectroscopy. Phys. Rev. Lett. **112**, 127002 (2014).

Acknowledgements We thank M. Ikeda and S. Kivelson for insightful conversations. We particularly appreciate the constructive and cordial discussions with K. Ishida and Y. Maeno about the implications of our findings, and K. Ishida for a series of private communications confirming that he reproduces them. A. P. acknowledges support by the Alexander von Humboldt Foundation through the Feodor Lynen Fellowship. Y. L. acknowledges a support by the 1000 Youth Talents Plan of China. N.K. acknowledges the support from JSPS KAKENHI (No. JP18K04715) and JST-Mirai Program (No. JPMJMI18A3) in Japan. This work was supported in part by the National Science Foundation (DMR-1709304) and by the Laboratory Directed Research and Development (LDRD) program of Los Alamos National Laboratory under Project No. 20170204ER.

Author Contributions A.P. and Y.L. contributed equally to this work. Y.L., A.P., A.P.M., and S.E.B. conceived and designed the experiments. D.S., N.K., F.J., C.W.H. and A.P.M. prepared the crystal. E.D.B. characterized the sample and performed the spin labeling. A.P. and Y.L. performed the NMR measurements, supported by Y.S.S. and A.C.. A.P., Y.L., C.W.H., A.P.M., S.R. and S.E.B. discussed the data, interpreted the results, and wrote the paper with input from all the authors. The time-synchronous reflection experiments were performed by S.E.B., A.P., and A.C.

Competing Interests The authors declare that they have no competing financial interests.

Correspondence Correspondence and requests for materials should be addressed to A. Pustogow (pustogow@physics.ucla.edu), Y. Luo (mpzslyk@gmail.com), or S. E. Brown (brown@physics.ucla.edu).

Main Figure Legends

Fig. 1: | **Strain dependence of the upper critical field of Sr$_2$RuO$_4$.** $B_{c2}(T \rightarrow 0, \varepsilon_{aa})$, determined by ac susceptibility measurements at base temperature, $T = 20$ mK. The increase with compressive strain peaks at ε_v, thus closely following the trend of the critical temperature T_c [4]. Inset: Strain gradients become more pronounced at higher strain reaching about $0.1\varepsilon_v$ at the van Hove singularity. More details in Methods.

Fig. 2: | **Knight shifts K vs. T, measured at the van Hove singularity ($\varepsilon_{aa} = \varepsilon_v$). a,** The NMR spectra at applied field $B_0 = 1.9980$ T and carrier f_0=11.54 MHz. Shown are three peaks corresponding to the O(1), O(2) and O(1$'$) sites (from left to right). Vertical lines indicate normal-state (solid) and $K = 0$ (dashed) frequencies. **b,** The associated Knight shifts K_{1b} and $K_{1'b}$

show a pronounced reduction below $T_c(B_0) = 2.6$ K (see lower inset and Methods), evidencing a drop of spin polarization M_s in the superconducting state. Upper inset: Experiments with varied pulse energy reveal a similar decrease of M_s below T_c for $\varepsilon = 0$; details below, see Fig. 3. Error bars correspond to 1/4 of the FWHM.

Fig. 3: | **Zero-strain ^{17}O NMR spectra of Sr$_2$RuO$_4$ for varying pulse energy.** **a**, Free induction decay (FID) measurements with varying pulse lengths $d_1 \leq d_{\pi/2}$ ($\pi/2$ corresponds to $E = 7.5$ μJ) were applied at the nominal base temperature $T_{MC} = 20$ mK, with $B_0 = 0.7107$ T, $f_0 = 4.137$ MHz. The O(1) and O(1$'$) peak shifts indicate smaller M_s for smaller E. For each site, the normal-state position is marked by the solid vertical lines; the estimated $K = 0$ position is the dashed line. **b**, Energy (equivalently: tip angle β) dependence of O(1), O(1$'$) shifts. Inset: The relative Knight shift reductions (normalized to normal state). Note that the three sites give comparable reductions; uncertainties for O(2) site are not shown. Error bars defined like in Fig. 2b.

Fig. 4: | **Transient effects following RF pulses, ε_{aa}=0.** A short RF pulse of duration d_1 is applied at time $\tau = 0$, followed by a low-power time-resolved cw measurement of the NMR tank circuit phase-sensitive reflected power, which is an RF equivalent to a complex ac susceptibility measurement. The data are presented as $\delta\rho_T$ vs. E, with $\delta\rho_T$ the changes to the reflection coefficient, and E the energy of the pulse. Both in-phase (IP) and quadrature (Q) parts of $\delta\rho_T$ are strongly impacted, at short times τ, for larger energies E. No similar time-dependence is observed when the sample is initially in the normal state.

represent.	basis func.	Nodes	TRSB	χ_{b0}/χ_N
A_{1u}	$\vec{d} = \hat{x}k_x + \hat{y}k_y$	No	No	1/2
B_{1u}	$\vec{d} = \hat{x}k_x - \hat{y}k_y$	No	No	1/2
A_{2u}	$\vec{d} = \hat{x}k_y - \hat{y}k_x$	No	No	1/2
B_{2u}	$\vec{d} = \hat{x}k_y + \hat{y}k_x$	No	No	1/2
B_{1g}	$\psi_d = k_x^2 - k_y^2$	vertical	No	0
B_{2g}	$\psi_d = k_x k_y$	vertical	No	0
E_u	$\vec{d} = \hat{z}\,(k_x \pm ik_y)$	No	Yes	1
E_u	$\vec{d} = k_z\,(\hat{x} \pm i\hat{y})$	horizontal	Yes	1/2
E_g	$\psi_{chiral} = k_z(k_x \pm ik_y)$	horizontal	Yes	0

Table 1: Irreducible representations for selected allowed $p-$ and $d-$ wave order parameters compatible with the D_{4h} symmetry of Sr_2RuO_4. The two E_u states identified belong to the same irreducible representation and can therefore coexist. Hence, the horizontal nodes of the E_u state with in-plane d-vector are not protected. Table entries for the ground state susceptibilities χ_{b0} apply to the case $\mathbf{B} \parallel \mathbf{b}$, and ignore spin-orbit coupling. Generally, the response vanishes in the case $\mathbf{B} \parallel \mathbf{d}$ [2,26,27]. In the presence of spin-orbit coupling (SOC), spin is no longer a good quantum number. While SOC is relevant to Sr_2RuO_4[28], the presence of an inversion center and time-reversal symmetry in its normal state leads to the conclusion that spin-orbit effects are important only near regions of accidental band degeneracy, which occupy a small fraction of the Brillouin zone, away from those areas at which the density of states is maximised. Consequently, taking SOC into account will not substantially affect the magnetic responses listed in the fifth column. χ_N is the normal-state spin susceptibility.

Methods

Experimental. The geometry of the experiment is shown in Extended Data Fig. 1. The crystal structure consists of layers of corner-sharing O octahedra with Ru ions at the center of each. In panel **a**, we illustrate the planar coordination (at the Y point of the Brillouin Zone) of hybridizing Ru and O orbitals predominating the quasi-2D γ band character. An in-plane magnetic field $B_0 \parallel b$ yields inequivalent O(1) and O($1'$) sites with distinct Knight shifts. Uniaxial deformation along the a-axis pushes the γ states at E_F towards the Brillouin zone boundary (Extended Data Fig.1b) giving rise to a van Hove singularity in the density of states [4,19].

High-quality single crystalline $\mathrm{Sr_2RuO_4}$ used for these measurements was grown by the floating-zone method as described elsewhere [8]. Smaller pieces were cut and polished along crystallographic axes with typical dimensions $3\times0.3\times0.15$ mm^3, with the longest dimension aligned with the $\mathbf{a}$-axis. ^{17}O isotope ($^{17}I = 5/2$, gyromagnetic ratio $^{17}\gamma_n = -5.7719$ MHz/T [29]) spin-labelling was achieved by annealing in 50% ^{17}O-enriched oxygen atmosphere at 1050 °C for 2 weeks [5]. The sample quality after annealing was confirmed by specific heat measurements which show $T_c \approx$1.5 K, essentially the same as before annealing [19].

A piezoelectric-type strain cell (Razorbill, UK) was employed to generate the uniaxial stress, and corresponding strain distortions along the $\mathbf{a}$-axis. Sample mounting between clamping plates included black Stycast 2850 (Loctite), with an effective compressive length about 0.9 mm. The strain values ε_{aa} were estimated by a pre-calibrated capacitive dilatometer, and could reflect considerable systematic overestimation. Previous estimates place $\varepsilon_v \simeq -0.6\%$. For NMR measurements, a small coil of $\sim$23 turns is made around the sample with 25 μm Cu wire. In Extended Data Fig. 1c we show the sample mounted in the strain cell where $\epsilon_{aa} \parallel a$ and $B_0 \parallel b$. The NMR coil was wrapped around the free part of the crystal, thus covering only the non-glued area that is subject to uniaxial stress. More information on strain-dependent NMR experiments on Sr_2RuO_4 can be found in Ref. [19].

NMR measurements were performed using a standard Hahn echo sequence with external magnetic field parallel to b-axis. Two samples in total were measured in this work, denoted as S1 and S2 respectively. S1 was measured at fixed strain ε_v ($T_c = T_c^{max}$=3.5 K) and carrier frequency f_0=11.54 MHz ($B_0 = 1.9980$ T) at temperatures spanning both sides of T_c. Two sets of measurements on S2 were carried out. First, a fixed carrier frequency $f_0 = 6.7$ MHz ($B_0 = 1.1573$ T) was chosen, for measurements at temperatures 25 mK (SC state) and 4.3 K (normal state), as a function of strain up to -0.58%. The second set of strain-dependent measurements in the superconducting state ($T = 25$ mK) was performed at $f_0 = 4.137$ MHz (B_0=0.7107 T), followed by a detailed study at zero strain. All measurements on S2 were performed using a dilution refrigerator (Oxford Kelvinox, UK) with the entire strain jig, including the Sr_2RuO_4 crystal, immersed inside the mixing chamber. The magnetic field value B_0 was referenced to the ^{3}He nuclear resonance condition at f_0. The mixing chamber temperature $T_{MC} = 20$ mK was confirmed by a measurement of the ^{63}Cu T_1 (in the coil), and exploiting the accepted value $T_1T = 1.27$ s-K.

NMR shift correction due to quadrupolar splitting. The NMR Knight shift, K, is generically defined as the percentage of the shift of resonance frequency with respect to a reference frequency f_{ref}=$^{17}\gamma_n B_0$, viz. f=$^{17}\gamma_n B_0(1 + K)$. However, an additional field-dependent correction is necessary for nuclei with I >1/2, due to quadrupolar coupling to the electric field gradient. On a relative scale, the angle-dependent correction to the central transition is more important in weaker fields. It was numerically evaluated by diagonalizing the nuclear spin Hamitonian

$$H_{tot} = H_Z + H_Q, \tag{1}$$

where

$$H_Z = h^{17}\gamma_n(1 + K)\mathbf{B_0} \cdot \hat{\mathbf{I}} \tag{2}$$

characterizes the Zeeman effect, and

$$H_Q = \frac{eQV_{zz}}{4I(2I-1)}[3\hat{I_z}^2 - \hat{\mathbf{I}}^\mathbf{2} + \eta(\hat{I_x}^2 - \hat{I_y}^2)] \tag{3}$$

is the quadrupolar term. Here h is Planck's constant, $\hat{\mathbf{I}}$=$(\hat{I}_x, \hat{I}_y, \hat{I}_z)$ is nuclear spin operator, Q is nuclear quadrupole moment, and η=(V_{xx}−V_{yy})/V_{zz} is the asymmetry parameter with V_{xx}, V_{yy} and V_{zz} being the components of the electric-field gradient (EFG) tensor.

For our magnetic field values used in this work, the calculated corrections for different ^{17}O sites are listed in Table 2 (in unit of kHz).

Upper critical field measurements and estimation of strain gradients. As summarized in Fig. 1, the upper critical field B_{c2} was determined at base temperature $T_{MC} = 20$ mK by measuring the field dependence of the power reflected from the NMR tank circuit. More specifically, the frequency is set close to the tune/match condition. Variations in the reflection coefficient $\delta\rho_T$ relate to changes in the complex load impedance. Consequently, the measurement is equivalent to an ac susceptibility experiment, and is sensitive to screening current changes that occur, for example, when the system is driven from the superconducting to the normal state by the magnetic field. B_{c2} is taken as the steepest slope at the transition midpoint, *i.e.*, the maximum of $d(\delta\rho_T)/dB_0$, as plotted in Extended Data Fig. 2a,b for the respective strain potential bias, U_{Piezo}. The 'onset' and 'lower end' values were defined as the kinks in the derivative $d(\delta\rho_T)/dB_0$ above and below B_{c2}, respectively. The superconducting transition exhibits considerable broadening with increasing compressive strain ε_{aa}. To model the apparently smeared transition, we assumed a Gaussian distribution of strains, and used the resulting distribution in B_{c2} to generate the solid magenta curves in Extended Data Fig. 2. The curves shown correspond to strain variations of 10% of the normalized value, $\varepsilon_{aa}/\varepsilon_v$ (see inset of Fig. 1). The approach provided a self-consistent method for estimating the relative importance of strain distributions, and suitably describes our observations.

Assessing the zero-strain position. The "zero-strain" condition attributed to the spectra shown in Fig. 3 was determined by taking the minimum in B_{c2} as a proxy. Note that since there is differential thermal contraction between strain device and sample, the strain-free condition needed to be assessed *in situ*. The determination was carried out in two steps. First, for a range of discrete values of piezo bias U_{piezo} ranging to positive and negative values about 0 V, $B_{c2}(U_{piezo})$ was determined using field sweeps and recording the reflected power, just as for the measurements described in Fig. 1, and Extended Data Fig. 2. Example sweeps are shown in Extended Data Fig. 3a,b, from which the minimum was found to be near $U_{piezo} = 0$ V. A more accurate determination was made by first setting the initial field to $B_{c2}(U_{piezo} = 0$ V). That is, the conditions were set to the transition midpoint as shown in the inset of Extended Data Fig. 3c. Then, changes in reflected power were recorded on sweeping U_{piezo} about zero. Here again, we found the zero-strain condition indistinguishable from $U_{piezo} = 0$ V. Thus, our experiments at low pulse energy indeed probe the superconducting properties of $\mathrm{Sr_2RuO_4}$ at zero strain.

Time-synchronous reflected power response. Our interpretation of the time-synchronous reflected power measurements were aided by comparable measurements carried out in variable field conditions, with the goal to contrast normal- and superconducting-state responses. Results are shown in Extended Data Fig. 4, where the applied pulse energies cover the range used for the NMR measurements. First consider panel **b**, which documents a measurement of the power reflected from the NMR tank circuit as the magnetic field is varied to a strength exceeding B_{c2}. The jump at 1.3 T corresponds to the transition to the normal state. The evolution at lower fields is presumably associated with the response of a changing vortex structure, including density and characteristic length scales. The vertical dashed line is the measurement field for the spectra shown in Fig. 3, $B_0 = 0.7107$ T. Both components of $\delta\rho_T$, in-phase (IP) and quadrature (Q), show a pronounced time dependence for large pulse energies. Our interpretation is that the sample under study is initially responding as though it is in the normal state. The relaxation back to the static superconducting state appropriate for the applied field occurs via a two-step relaxation process. First it is normal for $\tau \leq 100$ μs, followed by a slower relaxation on the order of a few milliseconds, while in the superconducting state. The horizontal dotted lines in Extended Data Fig. 4 indicate the values $\delta\rho_T(B_0)$ right above and below the superconducting transition, as well as the static state at 0.7107 T. The longer time is likely due to changing vortex structure, motion and creep. No such time dependence is observed if the sample is initially in the normal state.

Strain-dependent NMR shifts. The results from strain-dependent studies of the NMR Knight shifts are shown in Extended Data Fig. 5, with data from the superconducting state depicted by open symbols (equilibrium temperature 20 mK), and from the normal state indicated by solid symbols (equilibrium temperature 4.3 K) [19]. In addition to the results from Fig. 2 (green; $T = 20$ mK, $B_0 = 1.9980$ T), two different fields are shown for each temperature. The suppression of Knight shifts K in the superconducting state reaches about 80% for strain near ε_v in the case of B_0=0.7107 T (blue). The effect of superconductivity weakens on lowering the strain, as T_c and B_{c2} both decrease. Since the spectra are generated by the standard echo sequence for these data, the pulse energies are large – about $E \approx 10$ μJ, which is comparable to the top trace in Fig. 3 of the main text. Thus, the results at low and zero strain correspond to the normal-state shifts, which is very obvious in the 20 mK results at 1.1573 T (orange) that deviate from the 4.3 K data only for $\varepsilon_{aa} > \varepsilon_v/2$. While the reduction of K is generally more pronounced for 0.7107 T, also these data approach the normal-state values towards $\varepsilon_{aa} \to 0$. Evidently, the impact of the pulse energy decreases when the sample is strained because T_c increases and the heating effect is not sufficiently strong to drive the crystal to the normal state. The results appear to vary continuously with applied field and strain, hence they provide no indication for a first-order phase transition between different superconducting order parameter symmetries.

Method References

29. Hoult, D.I. Sensitivity of the NMR Experiment (eMagRes,Wiley Online Library, 2007)

Data Availability Statement

The data that support the findings of this study are available within the paper. Additional informations are available from the corresponding authors upon reasonable request.

Extended Data Figure Legends

Extended Data Fig. 1 | $\mathrm{RuO_2}$ plane, with $d_{xy} - p$ hybridizing orbitals and experimental setup. a, Depiction of Ru d_{xy}- and hybridizing O p-orbitals at the Y-point, which dominate formation of the γ band. NMR shifts are measured at the O(1) and O(1′) sites. **b,** Compressive a-axis stress shifts the γ band Fermi surface to the zone boundary at Y. **c,** Image of the strain device. The enlarged view highlights the $\mathrm{Sr_2RuO_4}$ single crystal mounted between piezoelectric actuators, with B_0 parallel to the b-axis and a-axis compressive stress, ε_{aa}. The NMR coil covers the free part of ≈ 1 mm length.

Extended Data Fig. 2 | Estimation of strain gradients. a, B_{c2} in Fig. 1 was determined from magnetic field sweeps of the tank circuit reflected power. The broadening of the superconducting transition was modeled by a Gaussian strain distribution of half-width $\delta\varepsilon/\varepsilon_{aa} \simeq 10\%$ (pink lines). **b,** The fitting curves also match with the corresponding derivative $d(\delta\rho_T)/dB_0$. For clarity, only a subset of the measured fields is shown.

Extended Data Fig. 3 | Tuning the crystal to zero strain. a, Measurements of the reflected power $\delta\rho_T$ at low strain indicate that B_{c2} has a minimum near $U_{Piezo} = 0$ V. **b,** The derivative $d(\delta\rho_T)/dB_0$ illustrates that B_{c2} associated with the largest rate of change at the transition midpoint first decreases when reducing compression ($U_{Piezo} = -20 \rightarrow 0$ V), followed by a slight increase upon tensile strain ($U_{Piezo} = 0 \rightarrow +12$ V). **c,** The coil impedance was measured at the transition midpoint (B_0 fixed at B_{c2} as indicated in inset), providing a sensitive measure of modifications upon changing strain. In intervals of 20 V or less, B_{c2} was determined by a field sweep and afterwards B_0 was set to the new transition midpoint. The results (solid blue squares) were corrected for the different B_0 yielding one half of a parabola centered around [-10 V;10 V], very similar to the strain dependence of T_c [3] (dashed black line).

Extended Data Fig. 4 | Transient effects associated with normal-state response. a, The transient components of reflected power are plotted as a function of pulse energy E and time τ after the pulse, cf. Fig. 4. **b**, The magnetic field dependence of reflected power was recorded at $E = 0.8$ μJ. The changes in $\delta\rho_T(B_0)$ on increasing B_0 from the measurement field (0.7107 T) to $B_0 > B_{c2}$ match well with the time-dependent recovery in **a**, as indicated by the horizontal dotted lines. Both channels (IP and Q) document a variation in $\delta\rho_T$ that results from a transition between normal and superconducting states around $\tau \approx 100$ μs.

Extended Data Fig. 5 | Strain dependence of ^{17}O Knight shifts in superconducting and normal states. Contrast of shifts in normal and superconducting states for strains covering the range $\varepsilon_{aa} = [0, \varepsilon_v]$. The top and bottom parts of the panel show the O1$'$ and O1 sites, respectively. Normal state is indicated by solid symbols (black and red) recorded at 4.3 K and two different field strengths [19]. Open symbols correspond to an equilibrium temperature of 20 mK, hence within the superconducting state for sufficiently high T_c realized by large strain and small magnetic field. Blue and orange symbols correspond to field strengths 0.7107 T and 1.1573 T, respectively. The results from $B_0 = 1.9980$ T are shown in green ($\varepsilon_{aa} = \varepsilon_v$; cf. Fig. 2).

B (T)	f_{ref} (MHz)	O(1)$_{\parallel}$	O(1$'$)$_{\perp}$	O(2)$_b$
0.7107	4.0980	1.0	57.5	43.0
1.1573	6.6798	0.8	36.0	26.7
1.9980	11.5323	0.5	20.4	15.6

Table 2: Quadrupolar corrections, in kHz, to central transition resonant frequencies $f = {}^{17}\gamma_n B_0$, for the three oxygen sites and field strengths applied along the b-axis. The listed values apply to the zero strain case, and we have used ${}^{17}\gamma_n$=5.772 MHz/T [19].