



Pressure-dependent magnetism of the Kitaev candidate Li_2RhO_3



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We use magnetization measurements under pressure along with ab initio and cluster many-body calculations to investigate magnetism of the Kitaev candidate Li_2RhO_3 . Hydrostatic compression leads to a decrease in the magnitude of the nearest-neighbor ferromagnetic Kitaev coupling K_1 and the corresponding increase in the off-diagonal anisotropy Γ_1 , whereas the experimental Curie-Weiss temperature changes from negative to positive with the slope of +40 K/GPa. On the other hand, spin freezing persists up to at least 3.46 GPa with the almost constant freezing temperature of 5 K that does not follow the large changes in the exchange couplings and indicates the likely extrinsic origin of spin freezing. Magnetic frustration in Li_2RhO_3 is mainly related to the interplay between ferromagnetic K_1 and antiferromagnetic Γ_1 , along with the weakness of the third-neighbor coupling J_3 that would otherwise stabilize zigzag order. The small J_3 distinguishes Li_2RhO_3 from other Kitaev candidates.

Honeycomb magnets with dominant Kitaev interactions are predicted to realize a spin-liquid state with emergent topological order and exotic excitations^{1,2}. Material realizations of this scenario are usually searched for among the low-spin d^5 compounds following the initial proposal by Jackeli and Khaliullin³. Whereas several honeycomb iridates and Ru^{3+} halides have been extensively studied experimentally^{4–6}, rhodates remain relatively less explored despite the fact that Rh^{4+} is isoelectronic to Ir^{4+} and well suited for realizing Kitaev exchange.

Lithium rhodate, Li_2RhO_3 , features a slightly deformed honeycomb lattice of the Rh^{4+} ions⁷ (see Fig. 1). Its silver analog, $\text{Ag}_3\text{LiRh}_2\text{O}_6$, can be prepared by an ion-exchange reaction⁸. Despite the rather similar structures of the honeycomb layer, these two compounds feature very different magnetic properties. Whereas the electronic state of Rh^{4+} in Li_2RhO_3 should be close to $j_{\text{eff}} = \frac{1}{2}$, akin to the typical Ir^{4+} compounds⁴, a departure from the $j_{\text{eff}} = \frac{1}{2}$ state has been detected in $\text{Ag}_3\text{LiRh}_2\text{O}_6$ by x-ray spectroscopy⁸. Li_2RhO_3 evades long-range magnetic order, but reveals a change in spin dynamics associated with spin freezing below 6 K^{9,10}, as confirmed by nuclear magnetic resonance and muon spectroscopies¹¹. By contrast, $\text{Ag}_3\text{LiRh}_2\text{O}_6$ develops long-range antiferromagnetic order below 90 K⁸, which is the highest Néel temperature among the d^5 honeycomb magnets reported to date. The differences between Li_2RhO_3 and $\text{Ag}_3\text{LiRh}_2\text{O}_6$ are far more drastic than between the corresponding iridates, $\alpha\text{-Li}_2\text{IrO}_3$ and $\text{Ag}_3\text{LiIr}_2\text{O}_6$, that reveal rather similar magnetic behavior with the long-range magnetic order below 15 K¹² and 8 K¹³, respectively. This comparison suggests

that rhodates may be more tunable by (hydrostatic or chemical) pressure compared to the iridates.

In the following, we explore this possibility and study pressure evolution of Li_2RhO_3 . X-ray diffraction experiments on this compound revealed the structural phase transition with the formation of linear Rh^{4+} chains above 6.5 GPa at room temperature¹⁴. It means that Li_2RhO_3 offers a broader pressure window for tuning magnetism of the Rh^{4+} honeycombs than different polymorphs of Li_2IrO_3 ¹⁵ that become nonmagnetic upon the structural dimerization transition already at 3.5–4.0 GPa at room temperature^{16–20} and at even lower pressures of 1.0–1.5 GPa on cooling^{21,22}. Here, we probe Li_2RhO_3 using magnetization measurements under pressure and follow the evolution of individual magnetic couplings in this material using ab initio and cluster many-body calculations. Previous quantum-chemistry studies reported Kitaev exchange as one of the leading terms in the Li_2RhO_3 spin Hamiltonian at ambient pressure²³.

Results

Magnetization under pressure

Figure 2a shows the inverse magnetic susceptibility H/M of Li_2RhO_3 measured as a function of temperature under various pressures. A temperature-independent term χ_0 , which stands for the residual part of the background from the pressure cell, has been subtracted for each pressure, respectively. At all pressures, the susceptibility monotonically increases upon cooling, similar to the ambient-pressure behavior reported in the literature^{9,11}. The high-temperature part of magnetic susceptibility can be fitted with the

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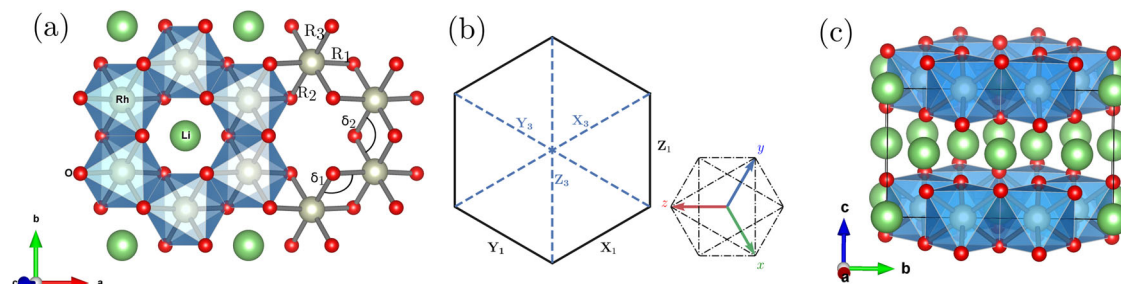
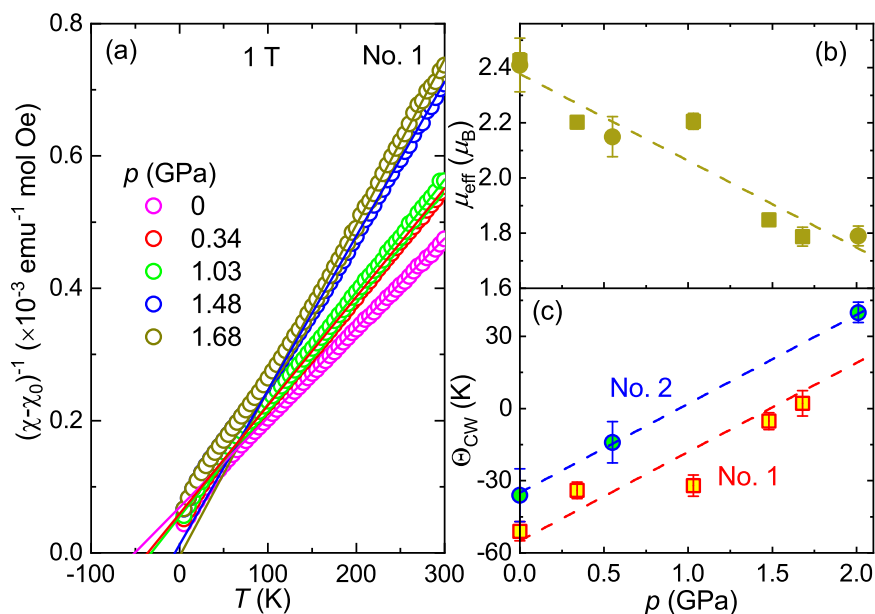


Fig. 1 | Structural details of Li_2RhO_3 . **a** Rh-honeycomb layer along the ab -plane showing the two symmetry allowed Rh-O-Rh angles and the definition of the Rh-O bonds. **b** Definition of the local coordinate reference frame x, y, z , and the bonds of interest for first and third neighbors. **c** Stacking of honeycomb layers in the Li_2RhO_3 structure.

Fig. 2 | Curie-Weiss analysis of Li_2RhO_3 under pressure. **a** Temperature-dependent inverse dc magnetic susceptibility H/M of Li_2RhO_3 measured at various pressures from 2 K to 300 K in a magnetic field of 1 T for run No. 1. Solid lines show the Curie-Weiss fits. Pressure evolution of **(b)** the effective moment μ_{eff} and **(c)** the Curie-Weiss temperature Θ_{CW} for run No. 1 (square symbols) and No. 2 (circle symbols). Dashed lines are linear fits.



Curie-Weiss law (solid lines), $\chi-\chi_0 = C/(T - \theta)$, where C is the Curie constant and θ is the Curie-Weiss temperature.

From the fits to the data between 150 K and 300 K, we find that the Curie constant and the associated paramagnetic effective moment weakly decrease with pressure, whereas the Curie-Weiss temperature increases and even changes sign from negative to positive (Fig. 2), indicating the growth of ferromagnetic interactions. At ambient pressure, the paramagnetic effective moment is around $2.4 \mu_B$ in agreement with the previous studies¹¹. It decreases with pressure and at 2 GPa reaches $1.8 \mu_B$, which is close to $1.73 \mu_B$ expected for the $j_{\text{eff}} = \frac{1}{2}$ state of Rh^{4+} .

At low temperatures, the smooth evolution of the magnetic susceptibility is consistent with the absence of any magnetic transition. The spin freezing reported below 6 K at ambient pressure^{9,11} can be tracked by the bifurcation of the magnetic susceptibilities measured under field-cooled (FC) and zero-field-cooled (ZFC) conditions in low applied fields. Such measurements become quite challenging under pressure because of the weak signal in low magnetic fields. Nevertheless, it was possible to track the FC/ZFC susceptibilities of Li_2RhO_3 in the applied field of 0.1 T up to 3.46 GPa (Fig. 3). The spin-glass like behavior of Li_2RhO_3 remains almost unchanged upon compression. The bifurcation of the FC/ZFC susceptibilities is seen at around 5.0 K at all pressures.

Microscopic magnetic model

Figure 4 shows the density of states for Li_2RhO_3 calculated on the full-relativistic (PBE+SO) level. Typically for a transition-metal oxide, the bands near the Fermi level are dominated by the d -states that are split into the t_{2g} and e_g manifolds by the octahedral crystal field. The $t_{2g} - e_g$ splitting is about

3.0 eV compared to the splitting of 2.0 eV in $\alpha\text{-RuBr}_3$ ²⁴ and 2.2 eV in $\alpha\text{-RuCl}_3$ ²⁵, in agreement with the higher negative charge of O^{2-} .

From the orbital energies obtained via the Wannier fit, we extract a small noncubic crystal-field splitting of only 13 meV, which is well below the spin-orbit coupling constant for Rh^{4+} . However, the t_{2g} states do not show the splitting into $j_{\text{eff}} = \frac{3}{2}$ and $j_{\text{eff}} = \frac{1}{2}$ bands known from the Ir^{4+} compounds. There is instead a three-peak structure reminiscent of Na_2IrO_3 ²⁶, with the peaks at -1.0, -0.7, and 0.0 eV. This splitting into three sub-bands is a fingerprint of the dominant off-diagonal hopping (t_2) that takes place between, e.g., the d_{yz} and d_{xz} orbitals and gives rise to the large Kitaev coupling²⁷. Our direct calculation of the exchange tensor confirms this assessment.

We define the exchange tensors in the Kitaev coordinate frame as

$$\mathbb{J} = \begin{pmatrix} J & \Gamma & \Gamma' \\ \Gamma & J & \Gamma' \\ \Gamma' & \Gamma' & J + K \end{pmatrix} \quad (1)$$

with four independent parameters (J, K, Γ , and Γ'). Technically, the X - and Y -bonds have a lower symmetry with six independent parameters²⁸, but our calculations show that the approximate form given by Eq. (1) is sufficiently accurate for these bonds as well, so it will be used in the following. The X - and Y -bonds are symmetry-equivalent but different from the Z -bonds. This difference is also relatively small at all pressures, as can be seen in the Supplementary Information. Therefore, in the rest of this work we will discuss the couplings averaged over the X -, Y -, and Z -bonds of the honeycomb lattice. We label these averaged couplings as $\bar{J}, \bar{K}, \bar{\Gamma}$, etc.

Figure 5 shows such averaged exchange couplings as a function of pressure. Li_2RhO_3 is dominated by the ferromagnetic nearest-neighbor Kitaev term K_1 that decreases in magnitude upon compression. The off-diagonal anisotropy Γ_1 increases under pressure, with the $|\bar{\Gamma}_1|/|\bar{K}_1|$ ratio changing from 0.34 at 0 GPa to 0.60 at 4.5 GPa. The nearest-neighbor Heisenberg coupling is weakly ferromagnetic and also increases in magnitude upon compression.

These pressure-induced changes in the nearest-neighbor couplings are well in line with the structural changes upon compression. Indeed, the Rh–O–Rh bond angles systematically decrease, leading to a reduction in the off-diagonal hopping t_2 and the weakening of the Kitaev term relative to the other terms of the exchange tensor²⁸. This mechanism appears to be generic for the Kitaev magnets that all show the reduction in the bond angles under hydrostatic pressure and the gradual suppression of the Kitaev term^{17,22,24}. The evolution of Li_2RhO_3 can also be followed on the phase diagram of the $J_1 - K_1 - \Gamma_1$ model (Fig. 6) where pressure systematically shifts the system away from the Kitaev limit located at $\varphi = 3\pi/2$.

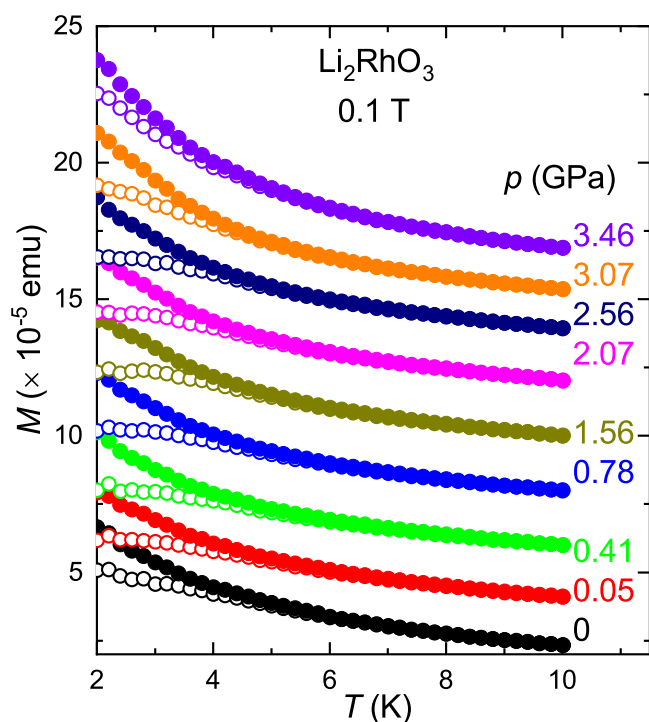


Fig. 3 | Temperature-dependent dc magnetic susceptibility $M(T)$ of Li_2RhO_3 measured at various pressures in a magnetic field of 0.1 T for run No. 3. The data are vertically offset for clarity. The solid symbols show the data collected upon field cooling (FC), whereas open symbols are the data collected upon zero-field cooling (ZFC).

Turning to the smaller terms in the spin Hamiltonian, we note that the off-diagonal anisotropy Γ' is below 1 meV at all pressures. Its negative sign should increase the proclivity of Li_2RhO_3 for zigzag order, as shown in the phase diagram of Fig. 6. However, the main term stabilizing the zigzag order is believed to be the antiferromagnetic third-neighbor coupling J_3 that has been estimated at about 1–3 meV in $\alpha\text{-RuCl}_3$ ^{4,29–31} and 2–6 meV in Na_2IrO_3 ^{28,32–34}. Surprisingly, the \bar{J}_3 of Li_2RhO_3 is quite small, about 0.15 meV according to our cluster many-body calculations. This suppression of \bar{J}_3 may be a result of the smaller spatial extent of the Rh 4d orbitals compared to the Ir 5d orbitals of the iridates, and of the O 2p orbitals compared to the Cl 3p orbitals of $\alpha\text{-RuCl}_3$. Interestingly, \bar{J}_3 obtained by the cluster many-body calculations is much lower than in the superexchange model. It means that the hoppings to the e_g orbitals yield ferromagnetic contributions that are strong enough to compensate for antiferromagnetic contributions from the intra- t_{2g} hoppings.

Discussion

Li_2RhO_3 remains a forgotten sibling of the much better known Kitaev iridates and Ru^{3+} halides. Although the first reports of its magnetic properties^{9,10} even preceded the discovery of $\alpha\text{-RuCl}_3$ as a Kitaev candidate, relatively little is known about its microscopic regime. The quantum-chemistry study of Li_2RhO_3 demonstrated a strong Kitaev coupling but also reported an unusually strong spatial anisotropy with $J_1^Z = -10.2$ meV having a different sign than $J_1^X = 2.4$ meV²³.

Our study advocates a more conventional microscopic scenario where spatial anisotropy plays only a minor role, and the couplings on the X/Y- and Z-bonds are qualitatively and quantitatively similar to each other. Moreover, the position of Li_2RhO_3 on the phase diagram of the extended Kitaev ($J_1 - K_1 - \Gamma_1$) model should resemble that of the Ru^{3+} halides, with the leading ferromagnetic Kitaev term $K_1 < 0$ and the subleading off-diagonal anisotropy $\Gamma_1 > 0$. The nearest-neighbor Heisenberg exchange, $J_1 < 0$, is relatively small at ambient pressure but becomes increasingly more important upon compression. This trend is corroborated by our magnetization measurements. Indeed, the powder-averaged Curie-Weiss temperature can be calculated as²⁸

$$\theta = -(3\bar{J}_1 + \bar{K}_1)/4k_B \quad (2)$$

and does not depend on $\bar{\Gamma}_1$. Whereas \bar{K}_1 decreases in magnitude with pressure, the leading trend is determined by the enhancement of ferromagnetic \bar{J}_1 that causes the increase in θ upon compression (Fig. 5g). Despite this good qualitative agreement, we note that the slope of the calculated pressure dependence is much lower compared to the experiment. Similar discrepancies have been reported in other Kitaev materials and ascribed to deviations from the simple Curie-Weiss law caused by the temperature dependence of the paramagnetic effective moment³⁵.

Although Li_2RhO_3 does not approach the Kitaev limit, the combination of $\bar{K}_1 < 0$ and $\bar{\Gamma}_1 > 0$ as the dominant terms in the spin Hamiltonian is a precondition for the strong frustration that has been comprehensively

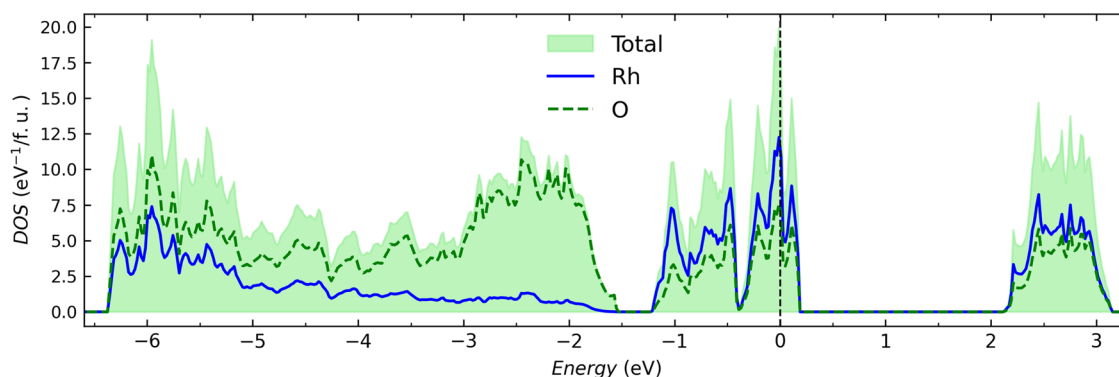
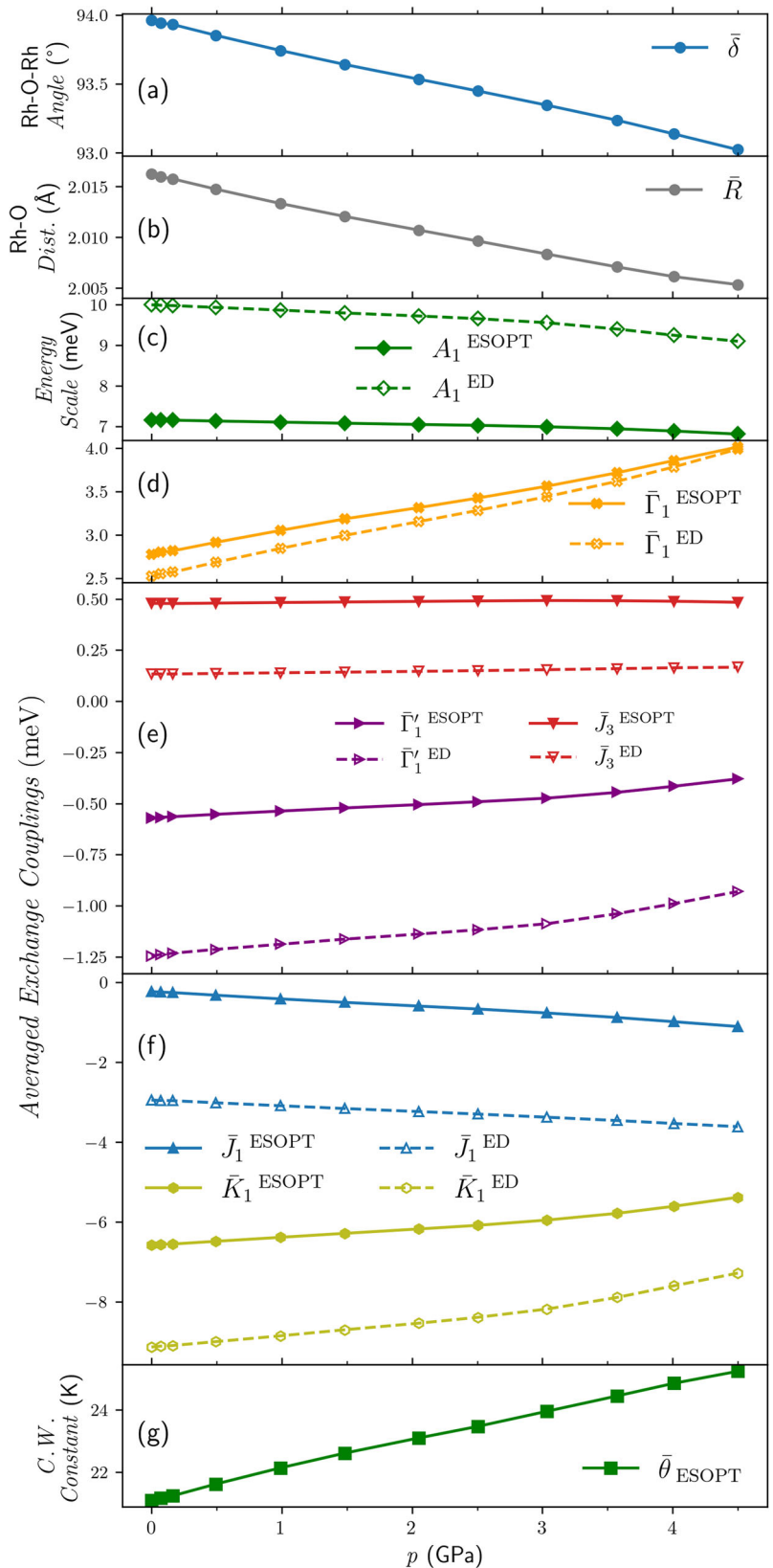


Fig. 4 | Full-relativistic (PBE+SO) density of states for Li_2RhO_3 calculated without spin polarization at ambient pressure. The Fermi level is at zero energy.

Fig. 5 | Pressure evolution of the averaged magnetic couplings in Li_2RhO_3 calculated by exact cluster diagonalization (ED) and second-order perturbation theory (ESOPT). **a** Averaged Rh-O-Rh angle $\bar{\delta}$. **b** Averaged Rh-O distance, \bar{R} . **c** Overall energy scale $A = (\bar{J}_1^2 + \bar{K}_1^2 + \bar{\Gamma}_1^2 + \bar{\Gamma}_1'^2)^{1/2}$. **d** Off-diagonal anisotropy $\bar{\Gamma}_1$. **e** Off-diagonal anisotropy $\bar{\Gamma}_1'$ and the third-neighbor coupling \bar{J}_3 . **f** Nearest-neighbor Kitaev (\bar{K}_1) and Heisenberg (\bar{J}_1) couplings. **g** Calculated pressure-dependent Curie-Weiss temperature. All lines are guides to the eye only.



studied in the context of the $K_1 - \Gamma_1$ model on the honeycomb lattice³⁶. This model connects the limits of the Kitaev spin liquid at large K_1 and classical spin liquid at large Γ_1 , whereas the intermediate region is often described as correlated paramagnet³⁶. With Li_2RhO_3 lying close to the $K_1 - \Gamma_1$ line on the phase diagram of the $J_1 - K_1 - \Gamma_1 - \Gamma_1'$ model, at least at ambient pressure,

it is not surprising that this material evades long-range magnetic order. Experimentally, we find spin freezing below 5 K that persists at least up to 3.46 GPa. Interestingly, the freezing temperature almost does not change, whereas individual exchange couplings are clearly affected by pressure. This observation suggests that spin freezing is driven by an extrinsic energy scale

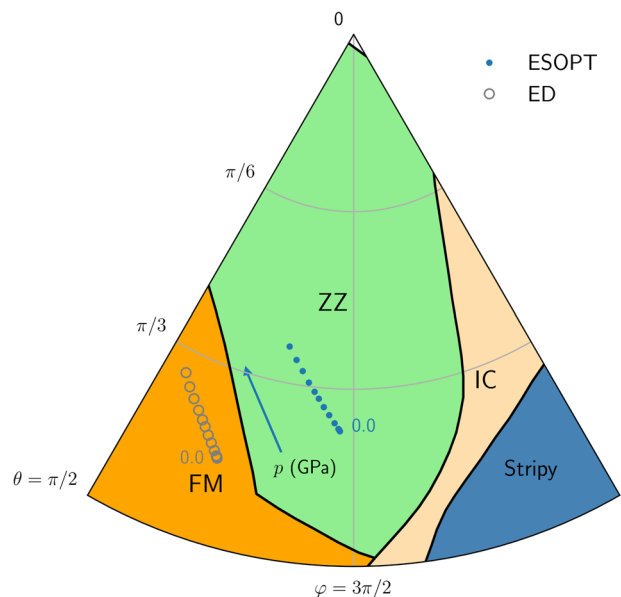


Fig. 6 | Li_2RhO_3 placed onto the classical phase diagram of the $J_1 - K_1 - \Gamma_1$ model⁴⁷ with $\Gamma'/A = -0.10$. The parameterization in polar coordinates corresponds to $J_1/A = \sin \theta \cos \varphi$, $K_1/A = \sin \theta \sin \varphi$, and $\Gamma_1/A = \cos \theta$ where θ is the radial part, φ is the angular part, and A is the overall energy scale defined in the caption of Fig. 5. The values averaged over the X -, Y -, and Z -bonds are used. Note that J_3 is not included. It is expected to stabilize zigzag order (ZZ) at the expense of the ferromagnetic order (FM).

and may be associated with the structural disorder arising from stacking faults^{10,16}. The high-pressure x-ray diffraction study of Li_2RhO_3 shows that the concentration of stacking faults is almost unchanged within the pressure range of our study¹⁴.

Although stacking faults are unavoidable in almost all Kitaev candidates because of their layered nature^{12,13,37,38}, this structural disorder will usually not preclude magnetic ordering. Na_2IrO_3 , $\alpha\text{-RuCl}_3$, and $\alpha\text{-RuBr}_3$ all show zigzag magnetic order, which is stabilized by Γ'_1 and J_3 . Whereas Γ'_1 is a comparably minor term across the whole family of the existing Kitaev materials, Li_2RhO_3 stands apart from the other Kitaev candidates in that its J_3 is unusually small. One can then interpret the absence of magnetic order in Li_2RhO_3 as the joint effect of the frustration caused by $K_1 - \Gamma_1$ and the weakness of J_3 . Additionally, the existing Li_2RhO_3 samples¹⁴ show about twice higher concentration of stacking faults compared to Na_2IrO_3 ³². This increased amount of structural disorder should increase the proclivity for spin freezing.

Finally, we note that our study supports the general trend of tuning Kitaev candidates away from the Kitaev limit by hydrostatic pressure¹⁵. One would then expect negative pressure to enhance the Kitaev term, reduce $\Gamma_1/|K_1|$, and bring the materials closer to the Kitaev limit. In this context, it is somewhat surprising that $\text{Ag}_3\text{LiRh}_2\text{O}_6$, the expanded version of the Li_2RhO_3 structure, not only shows magnetic ordering, but also features the highest Néel temperature among all Kitaev candidates reported to date⁸. The negative pressure effects in honeycomb rhodates may be nontrivial and clearly deserve a further dedicated investigation.

Methods

Sample synthesis and characterization

Polycrystalline samples of Li_2RhO_3 used in this work were previously characterized in refs. 11,14. Magnetization under pressure was measured with the same method as in ref. 39 using the gasket with the sample chamber diameter of 0.9 mm that can reach pressures up to 2 GPa. In order to reach higher pressures, the gasket was pre-indented, and pressures up to 3.46 GPa could be reached in run No. 3. A piece of Pb served to determine pressure from the temperature of its superconducting transition. Daphne oil 7373 was used as pressure-transmitting medium.

DFT and cluster many-body calculations

Density-functional band-structure calculations were performed in the FPLO code⁴⁰ using the Perdew-Burke-Ernzerhof (PBE) version of the exchange-correlation potential⁴¹. Hopping parameters were obtained by the built-in Wannierization procedure of FPLO⁴². Previous studies reported only the lattice parameters of Li_2RhO_3 as a function of pressure¹⁴, whereas oxygen positions had a large uncertainty due to limitations of the x-ray powder diffraction data. Therefore, we chose to fix the lattice parameters to their experimental values at each pressure and relaxed the atomic positions using DFT+ U calculations in FPLO, performing force optimization until the residual forces were less than 1×10^{-3} eV/Å. At ambient pressure, we obtained the Rh–O distances (R_1, R_2, R_3 in Fig. 1a) of 2.0395/1.9713/2.0379 Å, the Rh–Rh distances (Z, XY) of 2.9812/2.9315 Å, and the Rh–O–Rh bond angles (labeled as δ_1, δ_2) of 93.91/94.01°, which are in a good agreement with the experimental values⁷ of 2.033(6)/2.001(7)/2.029(3)/Å (Rh–O1/Rh–O1/Rh–O2), 2.950(4)/2.954(5) Å (Rh–Rh), and 94.16/93.29° (Rh–O1–Rh/Rh–O2–Rh). We also note that the experimental structural data for Li_2RhO_3 feature a weak Li/Rh site mixing⁷. This site mixing is caused by the interlayer disorder, such as stacking faults, whereas individual honeycomb layers are well-ordered⁸. Therefore, we used the fully ordered structural model in our calculations.

Magnetic couplings in Li_2RhO_3 are defined by the general spin Hamiltonian,

$$\mathcal{H} = \sum_{\langle ij \rangle} \mathbf{S}_i \mathbb{J}_{ij} \mathbf{S}_j \quad (3)$$

where \mathbb{J}_{ij} is the exchange tensor for the respective bond, and the summation is over bonds. The \mathbb{J}_{ij} components were determined by two complementary approaches. In the superexchange model, the hoppings within the t_{2g} manifold of the scalar-relativistic band structure are used to calculate the exchange couplings as described in ref. 28. Weak crystal-field splittings within the t_{2g} manifold and virtual processes involving the e_g states are neglected in this method.

Cluster many-body calculations allow a comprehensive treatment of the microscopic processes that underlie the exchange couplings. In order to calculate exchange couplings, we start by deriving the electronic Hamiltonian in terms of Rh 4d orbitals Wannier basis⁴². We obtain this Hamiltonian by performing fully relativistic (PBE+SO) calculations using a k -grid of $12 \times 12 \times 12$ and retaining the translational symmetry of the system. The obtained electronic Hamiltonian is exactly diagonalized on two-site clusters to get the low-energy eigenstates. These eigenstates are then projected to pure spin states by following the des Cloizeaux effective Hamiltonian method⁴³ to obtain the intermediate states which are finally orthonormalized by employing the symmetric (Löwden) approach⁴⁴. The advantage of the above described procedure is that it preserves all the symmetries and includes the effects of the non-cubic crystal-field splitting and nominally empty e_g orbitals that are neglected in the superexchange model.

In both cases, we used the same parameters of $U = 2.58$ eV and $J_H = 0.29$ eV for the on-site Coulomb repulsion and Hund's coupling, respectively, as determined for $\alpha\text{-RuCl}_3$ ⁴⁵. The spin-orbit coupling $\lambda = 0.15$ eV was used in the superexchange model.

Data availability

The experimental and computational data associated with this manuscript are available from ref. 46.

Code availability

All codes in this paper are available from the corresponding authors upon reasonable request.

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Author contributions

B.S. carried out the magnetization measurement under pressure. E.I.P., A.-A.T., R.D., and S.-M.W. performed the ab initio and cluster many-body calculations. F.F. synthesized the powder of Li_2RhO_3 . P.G. and A.-A.T. designed the project. All authors contributed to analyzing the data, discussions, and the writing of the manuscript.

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Competing interests

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