Unconventional magnetism in the 4d4-based $S = 1$ honeycomb system Ag$_3$LiRu$_2$O$_6$

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(Received 26 June 2017; revised manuscript received 18 January 2019; published 19 February 2019)

We have investigated the thermodynamic and local magnetic properties of the Mott insulating system Ag$_3$LiRu$_2$O$_6$ containing Ru$^{4+}$ (4d$^4$) for novel magnetism. The material crystallizes in a monoclinic $C2/m$ structure with RuO$_6$ octahedra forming an edge-shared two-dimensional honeycomb lattice with limited stacking order along the $c$ direction. The large negative Curie-Weiss temperature ($\theta_{CW} = -57$ K) suggests antiferromagnetic interactions among Ru$^{4+}$ ions, though magnetic susceptibility and heat capacity show no indication of magnetic long-range order down to 1.8 and 0.4 K, respectively. $^7$Li nuclear magnetic resonance (NMR) shift follows the bulk susceptibility between 120 and 300 K and levels off below 120 K. Together with a power-law behavior in the temperature-dependent spin-lattice relaxation rate between 0.2 and 2 K, it suggest dynamic spin correlations with gapless excitations. Electronic structure calculations suggest an $S = 1$ description of the Ru moments and the possible importance of further neighbor interactions as well as biquadratic and ring-exchange terms in determining the magnetic properties. Analysis of our muon spin rotation data indicates spin freezing below 5 K, but the spins remain on the borderline between static and dynamic magnetism even at 20 mK.

DOI: 10.1103/PhysRevB.99.054417

I. INTRODUCTION

Over the past few years, there has been a shift in focus from 3d-based systems to the exploration of 4d- and 5d-based ones due to the possibility of strong spin-orbit coupling (SOC) driving exotic magnetism [1–15]. The SOC is found to be very strong for 5d-based systems and could stabilize a Mott insulating state as well as other novel phases [1,2,6,12–15]. Issues such as the realization of the $J_{eff} = 1/2$ state for the $d^5$ configuration (half-filled) [2], possible realization of the Kitaev model [16] in $d^5$ Mott insulators [5,17], and the emergence of spin-liquid states in triangular lattice materials have been widely explored for Ir-based materials [6,7,12,18,19].

However, a very interesting scenario could arise for materials away from half-filling, such as four electrons in the $t_{2g}$ manifold. It has been proposed by Khalilullin [20] that, for oxide systems containing Ru$^{4+}$, Re$^{3+}$, Os$^{4+}$, or Ir$^{5+}$, there can often be comparable values of SOC ($\lambda \sim 50–200$ meV) and superexchange energy scales ($\Delta_{ex} \sim 50–100$ meV), which could give rise to excitonic magnetism and resultant novel phases. Recently, Meetei et al. [21] and Svoboda et al. [22] have worked further on this and suggested the possible formation of a spin-orbital liquid even in the absence of geometric frustration. Further, theoretical and experimental attempts have been made to realize this novel magnetism in Ir$^{4+}$-based perovskite NaIrO$_3$ [23], double perovskites Ba$_2$YIrO$_6$ and Sr$_2$YIrO$_6$ [24–30], and triple perovskite Ba$_3$ZnIr$_2$O$_9$ [31]. However, conclusive evidence of this novel magnetism is still elusive. This implies that one should explore materials with a lower SOC, and Ru$^{4+}$ materials might be a good starting point. Recent theoretical studies also proposed Ru-based materials as good candidates to search for excitonic magnetism [21,22].

In this report, we detail the structural, bulk, and local magnetic properties of the $t_{2g}^4$-based honeycomb system Ag$_3$LiRu$_2$O$_6$ [32] using x-ray diffraction, neutron diffraction, heat capacity, muon spin rotation ($\mu$SR) and nuclear magnetic resonance (NMR) techniques. The honeycomb structure decorated with any of the $d^5$ ions (Ru$^{4+}$, Re$^{3+}$, Os$^{4+}$, and Ir$^{5+}$) has been proposed to manifest novel physical properties [20]. In Ag$_3$LiRu$_2$O$_6$, structurally, Ru atoms give rise to a honeycomb geometry with the Li atom sitting at the center of the honeycomb. Our bulk data do not show any magnetic ordering down to 1.6 K in spite of strong antiferromagnetic interactions. A magnetic contribution to the specific heat is present compared to the nonmagnetic analog Ag$_3$LiTi$_2$O$_6$, but without any sharp anomaly. Static susceptibility deduced from the $^7$Li NMR line shift shows a plateau below 120 K and down to 150 mK. These signatures suggest that the static
spin correlations are absent or frozen out in the material. The $^7$Li nuclear spin-lattice relaxation rate $1/T_1$ decreases with decreasing temperature $T$ without any anomaly and displays a power law ($T^4$) behavior below 2 K. This is suggestive of magnetic moments remaining dynamic and the excitations being gapless. From our $\mu$SR measurements, $\text{Ag}_3\text{LiRu}_2\text{O}_6$ presents a spin-glass-like ground state with a transition temperature $T_g = 5.5(5)$ K though the spins display behavior which is at the borderline between static and dynamic even at 20 mK. Our ab initio electronic structure calculations indicate negligible SOC and point towards a ferromagnetic coupling between the three nearest neighbors of each Ru and antiferromagnetic further-neighbor couplings. This, coupled with deviations from the Heisenberg model, possibly results in frustration which might drive the observed behavior.

II. EXPERIMENTAL DETAILS

The polycrystalline samples of $\text{Ag}_3\text{LiRu}_2\text{O}_6$ and $\text{Ag}_3\text{LiTi}_2\text{O}_6$ (a nonmagnetic analog used for heat capacity analysis) were prepared in two steps. The precursor $\text{Li}_2\text{RuO}_3$ was synthesized by the solid state reaction route by firing stoichiometric amounts of $\text{Li}_2\text{CO}_3$ and Ru at 1000 °C for 12 hours in an alumina crucible, followed by another heating cycle at 950 °C for 24 hours after grinding the sample and mixing 10% excess $\text{Li}_2\text{CO}_3$. The nonmagnetic $\text{Li}_2\text{TiO}_3$ was prepared by firing a stoichiometric mixture of $\text{Li}_2\text{CO}_3$ and $\text{TiO}_2$ at 1000 °C. Having obtained single phase samples of the precursors $\text{Li}_2\text{RuO}_3$ and $\text{Li}_2\text{TiO}_3$, high purity $\text{AgNO}_3$ was mixed with each of the starting materials in the ratio 1:10 to prepare the final compositions of $\text{Ag}_3\text{LiRu}_2\text{O}_6$ and $\text{Ag}_3\text{LiTi}_2\text{O}_6$. The crucibles containing the mixture of materials in a 1:10 ratio were slowly heated to 300 °C in air and held at this temperature for 6 hours, followed by cooling to room temperature. The residual $\text{AgNO}_3$ and the reaction byproduct $\text{LiNO}_3$ were removed by washing the materials with water. X-ray diffraction measurements on the powder samples at room temperature were performed with a Panalytical Xpert Pro diffractometer using Cu-Kα radiation. Neutron diffraction data were taken on the DMC beamline at the Paul Scherrer Institute (PSI) at 300 and 1.6 K using a wavelength $\lambda = 2.4586$ Å.

Magnetization $M$ measurements as a function of applied field $H$ (0 to 90 kOe) and temperature $T$ (in the range 1.8 to 400 K) were performed using a Quantum Design SQUID VSM magnetometer. Zero-field cooled (ZFC) and field cooled (FC) magnetization measurements in a low field of 25 Oe were performed down to 1.8 K. The heat capacity $C_p(T)$ was measured with a Quantum Design physical property measurement system (PPMS) in various applied fields down to about 0.4 K. The $\mu$SR experiments were performed on a powder sample at PSI. In the high temperature range ($1.5 < T < 200$ K) we used the General Purpose Surface-muons (GPS) instrument. We mounted about 1 g of sample in a 15 mm × 15 mm Al envelope on a Cu fork. Therefore the sample stops the whole muon beam and we can neglect the experimental background. For the low-temperature regime (20 mK < $T$ < 17.5 K) we used the Low Temperature Facility (LTF) instrument. We glued about 1 g of powder with GE varnish on a silver plate to ensure thermal conductivity. Additionally, local probe nuclear magnetic resonance NMR measurements were performed on $\text{Ag}_3\text{LiRu}_2\text{O}_6$ at 300 K. The inset depicts the asymmetric peak (a characteristic of 2D structural order) around 20°. (b) Neutron diffraction data at 300 K (violet solid line) and 1.6 K (cyan solid line) with $\lambda = 2.4586$ Å. The encircled peak (dark yellow) at Bragg angle 31.5° is the asymmetric peak.

The polycrystalline samples of $\text{Ag}_3\text{LiRu}_2\text{O}_6$ and $\text{Ag}_3\text{LiMn}_2\text{O}_6$ (a nonmagnetic analog used for heat capacity analysis) were prepared in two steps. The precursor $\text{Li}_2\text{RuO}_3$ was synthesized by the solid state reaction route by firing stoichiometric amounts of $\text{Li}_2\text{CO}_3$ and Ru at 1000 °C for 12 hours in an alumina crucible, followed by another heating cycle at 950 °C for 24 hours after grinding the sample and mixing 10% excess $\text{Li}_2\text{CO}_3$. The nonmagnetic $\text{Li}_2\text{TiO}_3$ was prepared by firing a stoichiometric mixture of $\text{Li}_2\text{CO}_3$ and $\text{TiO}_2$ at 1000 °C. Having obtained single phase samples of the precursors $\text{Li}_2\text{RuO}_3$ and $\text{Li}_2\text{TiO}_3$, high purity $\text{AgNO}_3$ was mixed with each of the starting materials in the ratio 1:10 to prepare the final compositions of $\text{Ag}_3\text{LiRu}_2\text{O}_6$ and $\text{Ag}_3\text{LiTi}_2\text{O}_6$. The crucibles containing the mixture of materials in a 1:10 ratio were slowly heated to 300 °C in air and held at this temperature for 6 hours, followed by cooling to room temperature. The residual $\text{AgNO}_3$ and the reaction byproduct $\text{LiNO}_3$ were removed by washing the materials with water. X-ray diffraction measurements on the powder samples at room temperature were performed with a Panalytical Xpert Pro diffractometer using Cu-Kα radiation. Neutron diffraction data were taken on the DMC beamline at the Paul Scherrer Institute (PSI) at 300 and 1.6 K using a wavelength $\lambda = 2.4586$ Å.

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FIG. 2. (a) A unit cell of Ag$_3$LiRu$_2$O$_6$ with RuO$_6$ (Ru shown as pink balls) and LiO$_6$ (Li shown as blue balls) octahedra in the crystallographic $a$-$b$ plane. (b) A depiction of 2D edge sharing honeycomb lattice formed by Ru atoms in the $a$-$b$ plane with a Li atom sitting at the center of the honeycomb.

are in excellent agreement with the previously reported results [32]. In Ag$_3$LiRu$_2$O$_6$, Ru/Li ions coordinate with eight surrounding oxygen atoms and make RuO$_6$/LiO$_6$ octahedra [see Fig. 2(a)]. The RuO$_6$ octahedra connect in an edge-sharing fashion and give rise to a honeycomb network, and the Ru ions are best viewed as forming a two-dimensional (2D) honeycomb lattice in the $a$-$b$ plane [see Fig. 2(b)]. Note that although there is a unique Ru site, there are inequivalent O sites. As a result, there are two types of Ru-O-Ru bonds between a Ru and its three nearest neighbor Ru. As seen later, this results in two different couplings between a Ru and its nearest neighbors. The incorporation of Ag atoms into the primary material Li$_2$RuO$_3$ actually works as an intercalation between the Ru layers and essentially makes Ag$_3$LiRu$_2$O$_6$ a 2D system.

B. Magnetization

Figure 3 shows the dc susceptibility $\chi(T)$ of Ag$_3$LiRu$_2$O$_6$ measured in the $T$ range 2–600 K on a Quantum Design magnetic property measurement system (MPMS) with the oven option. The $\chi(T)$ data do not exhibit any anomaly in the $T$ range 2–600 K, though there are hints of a plateau around 100 K. Our neutron diffraction data, see Fig. 1(b), collected down to 1.6 K with wavelength $\lambda = 2.4586$ Å do not show any evidence of a phase transition either. A fit of the data to the Curie-Weiss law ($\chi = \chi_0 + C/T - \theta_{CW}$) in the $T$ range 300–600 K gives $\chi_0 = 1.7 \times 10^{-4}$ cm$^3$/mol Ru and the asymptotic Curie-Weiss temperature $\theta_{CW} = -57$ K. The negative $\theta_{CW}$ indicates the presence of antiferromagnetic coupling between Ru moments. Note that if $\chi_0$ is not left as a free parameter but fixed to a larger value, it yields a smaller $\theta_{CW}$ and a smaller Curie constant, though with a poorer fit. Measurements to even higher temperatures would have helped us obtain $\chi_0$ with better accuracy, but the sample degrades at higher temperatures. The value of the Curie constant $C$ is about 0.88 cm$^3$/K/mol Ru. This leads to an effective moment of 2.65$\mu_B$ which is slightly smaller than the expected spin-only value (for $S = 1$) of 2.83$\mu_B$. Magnetization under zero-field cooled (ZFC) and field cooled (FC) conditions was measured in a low field of 25 Oe. This is shown in Fig. 4. We find that there is a weak ZFC-FC bifurcation below about 3 K. In another sample of Ag$_3$LiRu$_2$O$_6$ (from a different batch) on which detailed $\mu$SR measurements (as well as neutron diffraction) were performed, the bifurcation is greater, and also occurred at a higher temperature of about 6 K. This could arise from a fraction of moments in the sample (extrinsic or intrinsic) which freeze.

C. Heat capacity

Heat capacity measurements were made to probe low-energy excitations associated with possible magnetism in the sample. Using data taken in a larger temperature range, Fig. 5(a) depicts the heat capacity ($C_p$) of Ag$_3$LiRu$_2$O$_6$ and structurally identical (nonmagnetic) Ag$_3$LiTi$_2$O$_6$ in the temperature range 0.4–40 K. The measured heat capacity for Ag$_3$LiRu$_2$O$_6$ does not show any significant dependence
on the magnetic field and remains featureless in the measured $T$ range. To extract the magnetic specific heat $C_m$ of $\text{Ag}_3\text{LiRu}_2\text{O}_6$, a procedure similar to that in Ref. [38] was employed. The heat capacity of nonmagnetic $\text{Ag}_3\text{LiTi}_2\text{O}_6$ was measured. The ratio of the Debye temperatures of the Ru compound and the Ti compound, $\frac{\theta(D_{\text{Ru}})}{\theta(D_{\text{Ti}})}$, was determined using the procedure of Ref. [38]. The temperature data of $\text{Ag}_3\text{LiTi}_2\text{O}_6$ was multiplied by the ratio of the Debye temperatures $\frac{\theta(D_{\text{Ru}})}{\theta(D_{\text{Ti}})} = 0.95$ before the specific heat of $\text{Ag}_3\text{LiTi}_2\text{O}_6$ was subtracted from the total specific heat of $\text{Ag}_3\text{LiRu}_2\text{O}_6$. The magnetic specific heat $C_m$ thus obtained is shown in Fig. 5(b). At low $T$, a power-law behavior is seen with an exponent of about 1.65 in zero applied field. The calculated entropy change ($\Delta S$) for $\text{Ag}_3\text{LiRu}_2\text{O}_6$, shown in Fig. 5(c), is estimated to be about 11% of 9.12 J/K mol Ru expected for $S = 1$. The power-law $T$ dependence of $C_m$ and the large quenching of $\Delta S$ supports the realization of a highly degenerate ground state, which is presumably gapless.

D. $^7\text{Li}$ NMR

NMR, being a local probe, is instrumental in identifying the change in magnetization at a local level. We performed $^7\text{Li}$ (nuclear spin $I = \frac{3}{2}$, gyromagnetic ratio $\frac{\gamma}{\mu_B} = 16.546$ MHz/T) NMR spectra measurements (echo integral at variable frequency) at various temperatures from 300 down to 150 mK. Data were obtained in two ways: (i) in a fixed field of $H = 93.954$ kOe the echo integral was obtained as a function of the frequency in the temperature range $300$ to $80$ K, and (ii) at a fixed frequency of 95 MHz the echo integral was obtained as a function of the field of the $T$ range $120$ to $150$ mK. The spectra are displayed together in Fig. 6 after scaling the $x$ axis of the frequency sweep data with the gyromagnetic ratio of $^7\text{Li}$ to obtain it in field units corresponding to the frequency of the field sweep measurements. The $^7\text{Li}$ NMR spectra were found to be asymmetric throughout the measured temperature range, having (i) a main peak, which qualitatively displays a variation with temperature, and (ii) a shoulder on the higher field side which is centered around the zero-shift position, and which remains almost unaffected in the entire temperature range (see Fig. 6). The appearance of this shoulder in $^7\text{Li}$ NMR powder spectra is most likely due to the anisotropy of the hyperfine field. Any significant Li/Ru antisite structural disorder is ruled out by our x-ray analysis. In the light of this anisotropy, the static susceptibility was estimated by extracting the $K_{\text{iso}}$ (powder averaged line shift) as a function of $T$ by matching the experimental $^7\text{Li}$ NMR spectra with the simulated one. The $K_{\text{iso}}$ follows the bulk susceptibility data, suggestive of a significant hyperfine coupling between Ru and Li atoms. The $K_{\text{iso}}$ becomes nearly $T$ independent (or perhaps weakly decreases) below about $120$ K as seen in Fig. 7(a). So the low-temperature rise in the bulk susceptibility appears to be driven by some extrinsic Curie contributions. A finite shift at the lowest temperature suggests gapless spin excitations. Note, however, that NMR measurements are made in a magnetic field and a finite shift could result from the closing of the gap due to the field, but the zero-field heat capacity data exclude the possibility of a gap. The width of the spectrum remains unchanged below $T \approx 2$ K (see Fig. 6). The hyperfine coupling constant $A_{hf}$ follows the relation $K_{\text{iso}} = K_{\text{chem}} + \frac{A_{hf}}{N_A\mu_B} \chi_{\text{spin}}$ ($K_{\text{chem}}$ is the chemical shift, $N_A$ is the Avogadro number, $\mu_B$ is the Bohr magneton, and $\chi_{\text{spin}}$ is the bulk susceptibility). From the slope of the $K_{\text{iso}}$ vs $\chi_{\text{spin}}$ plot, $A_{hf}$ was found to be $2.34(13)$ kOe/$\mu_B$ with $K_{\text{chem}} = 0.03(1)%$, as shown in the inset of Fig. 7(a). The value of the hyperfine coupling will turn out somewhat larger if the fitting range is limited to higher temperatures.

The $^7\text{Li}$ NMR spin-lattice relaxation rate $(1/T_1)$ measurements were performed with the saturation recovery method to study the low-energy spin dynamics or to probe the

FIG. 5. (a) Heat capacity for $\text{Ag}_3\text{LiRu}_2\text{O}_6$ at different fields (various symbols) and for nonmagnetic analog $\text{Ag}_3\text{LiTi}_2\text{O}_6$ at zero field (solid line) are shown as functions of temperature. (b) Magnetic specific heat $C_m$ as a function of $T$ for $\text{Ag}_3\text{LiRu}_2\text{O}_6$ with $H = 0, 30, 60$, and $140$ kOe. (c) Entropy change at $H = 0$ Oe for $\text{Ag}_3\text{LiRu}_2\text{O}_6$.

FIG. 6. $T$ dependence of $^7\text{Li}$ NMR (normalized) spectra for $\text{Ag}_3\text{LiRu}_2\text{O}_6$. The shift is seen to be temperature independent from $120$ K down to about $150$ mK. Note that the spectra above $121$ K were actually obtained from the echo integral at various frequencies in a fixed field of $93.94$ kOe. For these spectra, the $x$ axis was then converted to field units to compare with the lower temperature data which were obtained by sweeping the field at a fixed frequency of $95$ MHz.
The short component (\(m_{\text{short}}\)) is the intrinsic contribution. However, both the long and the short \(T_1\) components follow the same qualitative behavior. Figure 7(b) illustrates the variation of \(1/T_{1L}\) and \(1/T_{1S}\) in the range 0.3–210 K. A gradual decrease is seen down to 30 K with a broad plateau around 2 K which is followed by a falloff with a \(T^4\) power law at lower \(T\). The broad maximum is not due to any spin freezing, as the \(^7\)Li NMR line remains unbrodened all the way from 120 K down to 150 mK. The \(T^4\) variation of \(1/T_1\) below 2 K suggests that the spins remain dynamic and that the excitations are gapless. The data could be fit to a gapped behavior with a gap of about 3 K but our heat capacity data show a power-law decrease. Such power-law behavior is also seen in other spin-liquid candidate materials [12,39].

### E. \(\mu\)SR

As mentioned before, for the GPS experiments, the background signal can be neglected. For the LTF data (20 mK < \(T < 17.5\) K) we need to estimate the background signal Bgd. At 3 K, we have data from the GPS as well as the LTF beamline. We then vary Bgd for the LTF data so that the background subtracted data for LTF (at 3 K) coincides with the GPS data at 3 K. This yields Bgd = 0.014(1). For clarity, and to directly compare the GPS and LTF data, the raw curves are presented in terms of polarization, \(P(t)\), where

\[
P(t) = \frac{A(t) - \text{Bgd}}{A_0 - \text{Bgd}}.
\]

We present first the zero-field (ZF) experiments that we have performed from 200 K down to 20 mK (Fig. 9 left). From these data, it is clear that there is a transition in the whole compound between 20 K and 1.56 K. Indeed, at high temperature, in the paramagnetic regime, the depolarization is quite slow and can be attributed to the influence of Li magnetic nuclei. We assumed that the depolarization at 200 K is of a Gaussian scale, and the depolarization at long time is close to \(1/3\). This is characteristic of frozen or quasistatic magnetism. Nevertheless, the lack of spontaneous oscillations could be directly linked to an absence of long range ordered magnetism. Therefore, our \(\mu\)SR experiment reveals a short range ordered spin-glass-like ground state or a dynamic ground state with a large distribution of fields. To have better insight on the ground state probed by \(\mu\)SR, we fitted the data with an equation containing two relaxing components which has been used for other spin-glass systems [42,43]:

\[
P(t) = f_{\text{iso}}(\frac{1}{2} e^{-2\lambda_{\text{iso}}} + \frac{1}{2} e^{-2\lambda}) + (1 - f_{\text{iso}})P_{200\,\text{K}} e^{-2\lambda}.
\]

This yields \(\sigma_{\text{Nucl}} = 0.156(1) \, \mu\text{s}^{-1}\) which is directly linked to the nuclear field \(H_{\text{Nucl}}\) via \(\sigma_{\text{Nucl}} = \gamma_\mu H_{\text{Nucl}}\), where \(\gamma_\mu = 2\pi \times 135.5 \, \mu\text{s} \, \text{T}^{-1}\) is the gyromagnetic factor of the muons. We found \(H_{\text{Nucl}} = 1.83(2) \, \text{G}\), which is in the usual range of nuclear field values. At low temperatures, the depolarization is rather quick, on the 0.1 \(\mu\text{s}\) scale, and the depolarization at long times is close to \(1/3\). This is characteristic of frozen or quasistatic magnetism.
FIG. 9. Left: Polarization versus time at selected temperatures in zero field. The circles are the raw data and the lines are the fit with Eq. (3). Right: Depolarization rates versus temperature. The black circles are \( \lambda \) (left scale) and the red ones are \( \lambda_{\text{Fast}} \) (right scale). Inset: Frozen fraction versus temperature. The solid circles are the GPS results, the open circles are the LTF results. The dashed line represents the transition temperature \( T_g \).

where \( f_{\text{Fro}} \) is the fraction of sample in the frozen state, \( \lambda_{\text{Fast}} \) accounts for the fast depolarization at short time and represents the distribution of quasistatic fields in the sample, and \( \lambda \) accounts for the electronic magnetism and could be linked to its fluctuations. Note that we also tried to fit the data using the dedicated spin glass function [44] as well as dynamic and static Kubo-Toyabe functions, which resulted in poorer fits than with Eq. (3).

The results are presented in Fig. 9 right. The small differences between GPS and LTF likely arise from the difficulty to fully characterize Bgd in LTF. The frozen fraction increases at 10 K, getting close to 1 below 3 K. Therefore, the transition is not due to an impurity but presents a bulk character. Further, from the depolarization rate \( \lambda \) we can determine the transition temperature \( T_g \). Indeed, \( \lambda \) possesses a peak around 5.5(5) K, which is characteristic of a transition to frozen magnetism. Moreover, there is a very small plateau at 0.11(1) \( \mu s^{-1} \) which could be related to small fluctuations of the magnetism below 1 K and could be due to a quasistatic order. Further, below this temperature, \( \lambda_{\text{Fast}} \) presents a plateau around 25(2) \( \mu s^{-1} \) which is due to the distribution of the quasistatic fields. From this value, one can directly compute the field distribution \( \Delta = \lambda_{\text{Fast}} / \gamma \mu = 290(30) \) G.

To distinguish between static and dynamic magnetism we applied several longitudinal fields in the direction of the muon beam. Indeed, in the case of static magnetism a longitudinal field which is 10 times the field distribution should decouple the muons, whereas in the dynamic case a longitudinal field 50 times stronger than the field distribution is needed [45]. At 20 mK, the muons are almost fully decoupled under a field of 0.5 T (\( \sim 17 \times \Delta \)) (Fig. 10) indicating that the magnetism observed below 5 K is at the borderline between static and dynamic behavior. Therefore, due to the lack of spontaneous oscillations and the decoupling experiment, \( \text{Ag}_3\text{LiRu}_2\text{O}_6 \) presents a spin-glass-like ground state with a transition temperature \( T_g = 5.5(5) \) K based on the \( \mu \)SR analysis.

**F. Electronic structure calculations**

In order to obtain further insight into the possible origin of the observed magnetic behavior, given the apparent absence...
of geometric frustration, we have carried out electronic structure calculations using the full-potential linearized augmented plane wave (FP-LAPW) [46,47] plus local orbitals method using the Wien2K code [48]. Exchange and correlation effects are treated within generalized gradient approximation (GGA) [49] of Perdew, Burke, and Ernzerhof including Hubbard $U$ [50] and spin-orbit coupling (SOC). The double counting correction in the GGA+$U$ formalism is taken into account around the mean field approximation [51]. The calculations were done with usual values of $U$ and $J_H$ [52] chosen for Ru: $U = 3.0$ eV and Hund’s coupling $J_H = 0.7$ eV. The calculations were also checked for various other values of $U$. In order to achieve the convergence of energy eigenvalues, the kinetic energy cutoff was chosen to be $R_{MT}$ denotes the smallest atomic sphere radius and $K_{max}$ gives the magnitude of the largest $K$ vector in the plane-wave expansion in the interstitial region. The Brillouin zone integrations were performed with an $8 \times 8 \times 6 k$-points mesh. The total energies necessary for the calculation of symmetric exchange interactions [53] were calculated using density functional theory (DFT) and the projector augmented-wave (PAW) method as encoded in the Vienna $ab$ initio simulation package (VASP). The kinetic energy cutoff of the plane wave basis was chosen to be 600 eV and a $\Gamma$ centered $4 \times 4 \times 6 k$ mesh has been used for Brillouin zone (BZ) integration.

The spin polarized density of states in the framework of GGA+$U$ with $U = 3.0$ eV and $J_H = 0.7$ eV in the ferromagnetic configuration [54] is shown in Fig. 11. The system is found to be insulating, with the majority Ru $t_{2g}$ spin states completely occupied while the minority $e_g$ states are only partially occupied. The $e_g$ states for both the spin channels are completely empty. As a consequence of the monoclinic distortion promoted by Jahn-Teller active Ru$^{4+}$ ions the degeneracy of the Ru $t_{2g}$ states is completely lifted, which on inclusion of the Hubbard $U$ introduces a gap in the minority spin channel. The total moment is calculated to be $4\mu_B$ (per formula unit) with moments at Ru and O sites being $1.16\mu_B$ and $0.18\mu_B$ respectively, suggesting strong hybridization of the Ru with oxygen states. Next, we included spin-orbit coupling in our calculation. The total moment was then calculated to be $3.97\mu_B$ with spin and orbital moments at the Ru site $1.15\mu_B$ and $0.03\mu_B$, respectively. The small orbital moment suggests that a spin-only description is valid and neither the LS nor the $jj$ coupling schemes should be employed. These calculations suggest that the system is far away from the $J = 0$ limit and the $S = 1$ description of the system is more appropriate. To understand the absence of an ordered state, we calculated the first, second, and third neighbor symmetric exchange interactions, mapping the density functional total energies obtained using the Vienna $ab$ initio simulation package (VASP) within the projector-augmented wave (PAW) method onto the Heisenberg model following the method proposed in [53]. The magnitude and the sign of the symmetric exchange interactions are found to be very sensitive to the chosen configuration for calculation and the size of the simulation cell, suggesting the importance of the higher order magnetic interactions (biquadratic and four-spin ring couplings), as the usual approximation of the Hubbard model reducing to the Heisenberg model in the limit of large $U$ may not be applicable here [55]. The calculations have been done (with the experimental structural parameters) for several spin configurations using simulation cells of different sizes. Our calculations reveal that the nearest-neighbor exchange interactions $J_a$ and $J_b$ are ferromagnetic while the further-neighbor interactions (such as $J_c$, $J_d$, $J_e$, and $J_f$) are antiferromagnetic. On the other hand, if we relax the structure and then calculate the couplings, the nearest and the next-nearest neighbor interactions turn out to be antiferromagnetic. With a larger number of antiferromagnetic further-neighbour couplings, one can still recover a negative $\theta_{CW}$ as observed experimentally. This, coupled with the ring exchange and biquadratic couplings, introduces frustration in the system and possibly drives the system away from order.

IV. DISCUSSION

From the wide range of measurements that we have presented together with first-principles electronic structure calculations, let us now look at things in perspective. Usual bulk susceptibility measurements did not show any signatures of long-range order down to 1.8 K. Heat capacity measurements (zero or nonzero applied field) also do not evidence any long-range order down to 1.8 K. $^7$Li NMR measurements on the same sample did not show any line broadening nor any peak in the spin lattice relaxation rate down to 0.15 K. In fact, the $^7$Li shift (which probes the intrinsic susceptibility), starting at room temperature, increases with decreasing temperature. This suggests that there is magnetism in the system which must come from Ru$^{4+}$ ions ($4d^4$). Note that we tried to fit the $T$ variation of the intrinsic susceptibility to the formula given by Kotani [56] for the Van Vleck susceptibility of $d^4$ systems. This gave rise to very poor fits. The apparent agreement with the Kotani formula for the susceptibility of $\text{Ag}_3\text{LiRu}_2\text{O}_6$ in Ref. [57] is misleading, as that work seems to have considered only the $T$ region where the susceptibility is nearly constant. Also, our calculations suggest that this is a spin-only moment. With a continued decrease in temperature, the $^7$Li shift levels off below about 120 K and remains so
down to 150 mK. The $^7$Li NMR linewidth does not show any divergence either, and remains constant down to 150 mK. All the above suggests that the magnetism in this system somehow gets quenched below 120 K and no order sets in. Note that the NMR measurements are in a field of about 57 kOe, which corresponds to a significant energy scale in our low-$T$ regime (below 5 K or so). Let us now look at the results of low- and zero-field measurements. The magnetic heat capacity shows no special features other than a power-law variation at low $T$ (below about 4 K) and a broad maximum around 10 K. The low-field (25 Oe) ZFC and FC magnetizations do show some bifurcation at low $T$ which is sample dependent. The sample on which we performed the heat capacity and all the NMR measurements showed a weak ZFC-FC bifurcation (less than 10%) below about 3 K. When the same sample was measured in $\mu$SR (zero field), we found evidence of freezing around 3.5 K. On the other hand, the sample on which we did detailed $\mu$SR measurements (presented here) showed a larger ZFC-FC bifurcation and around 7 K. This sample shows a freezing of moments below about 5.5 K from $\mu$SR. The question now is how to reconcile the $\mu$SR data with the NMR, susceptibility, and heat capacity data. It appears that the zero-field $\mu$SR and low-field magnetization results are consistent with each other. For the zero-field heat capacity, the lack of entropy as well as the broad peak around 10 K and the power-law behavior at low temperatures could perhaps arise in the case of a spin glass state. The differing NMR results might come from a field effect. The $^7$Li NMR linewidth should have shown a critical divergence (or at least a significant increase) around the freezing temperature. The absence of this suggests that the applied field prevents the formation of static moments. Nevertheless, these results are very similar to the one obtained in another honeycomb compound, Li$_2$RhO$_3$ \cite{34}. Note also that the magnetism observed by us in $\mu$SR below 5 K is at the borderline of static and dynamic. Therefore, even if the $\mu$SR experiments rule out the possibility of a quantum spin-liquid ground state due to the presence of frozen magnetism below 5.5(5) K, this compound does not present a regular spin-glass behavior.

\section*{V. CONCLUSIONS}

In summary, we investigated the structural, thermodynamic, and local magnetic properties of the honeycomb-structure-based quantum material Ag$_3$LiRu$_2$O$_6$ by performing x-ray diffraction, neutron diffraction, susceptibility, heat capacity, and $^7$Li NMR measurements. The presence of an asymmetric peak in both x-ray and neutron diffraction profiles is suggestive of a 2D structural ordering (honeycomb) in the $a$-$b$ plane. The $\chi(T)$ data indicate a strong antiferromagnetic coupling between the Ru moments without showing any anomaly down to 2 K, and the neutron diffraction carried out down to 1.6 K does not detect any magnetic order. Heat capacity displays a $\sim T^{1.7}$ dependence at low $T$, and the deduced entropy change was found to be highly suppressed: $\Delta S \sim 11\%$ of that for an ordered spin-1 system. $^7$Li NMR powder spectra measurements helped in extracting the intrinsic susceptibility of Ru moments, and a leveling off of the NMR line shift was found for $T \lesssim 120$ K. Our electronic structure calculations provide a clue to the origin of the observed susceptibility saturation in this system, which (in principle) is not geometrically frustrated. Our study suggests that the magnetism here is not excitonic in origin. We propose that the frustration induced by further-neighbor couplings and a deviation from the simple Heisenberg model is responsible for the lack of LRO in this system. While spin freezing below about 5 K is evidenced from our zero-field $\mu$SR data, from the longitudinal field decoupling experiments, the moments are at the borderline between static and dynamic even at 20 mK. It needs to be explored whether defects such as stacking faults finally drive the system to a frozen state and whether the pristine system might be a spin liquid.

\section*{ACKNOWLEDGMENTS}

This work is partially based on experiments performed at the Swiss spallation neutron source SINQ, Paul Scherrer Institute, Villigen, Switzerland. We thank Department of Science and Technology (DST), Government of India for financial support through the BRICS project Helimagnets. R.K. acknowledges Council of Scientific and Industrial Research (CSIR) (India) and IRCC (IIT Bombay) for support via research fellowships to carry out this research work. P.M.E. acknowledges CSIR, INDIA for providing financial support under a CSIR-SRF fellowship (Grant No. 31/52(14)2k17), A.V.M. thanks the Alexander von Humboldt Foundation for support. Work at Augsburg was supported by the Deutsche Forschungsgemeinschaft (DFG) through the collaborative research center TRR80 (Augsburg/Munich). A.A.G. acknowledges CSIR, INDIA for providing financial support under a CSIR-SRF fellowship (Grant No. 31/52(14)2k17), A.V.M. thanks the Alexander von Humboldt Foundation for support. Work at Augsburg was supported by the Deutsche Forschungsgemeinschaft (DFG) through the collaborative research center TRR80 (Augsburg/Munich). A.A.G. acknowledges financial support from the RFBR under Grant No. 17-52-80036. We thank Kedar Damle for useful discussions and Dana Vieweg for technical help.

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