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Spin-liquid behavior of the three-dimensional magnetic system $\text{Ba}_3\text{NiIr}_2\text{O}_9$ with $S = 1$

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The quantum spin liquid (QSL) is an exotic phase of magnetic materials where the spins continue to fluctuate without any symmetry breaking down to zero temperature. Among the handful reports of QSL with spin $S \geq 1$, examples with magnetic ions on a three-dimensional (3D) magnetic lattice are extremely rare since both larger spin and higher dimension tend to suppress quantum fluctuations. In this work, we offer a new strategy to achieve 3D QSL with high spin by utilizing two types of transition metal ions; both are magnetically active but located at crystallographically inequivalent positions. We design a 3D magnetic system $\text{Ba}_3\text{NiIr}_2\text{O}_9$ consisting of interconnected corner-shared NiO_6 octahedra and face-shared Ir_2O_9 dimer, both having triangular arrangements in a - b plane. X-ray absorption spectroscopy measurements confirm the presence of Ni^{2+} ($S = 1$). Our detailed thermodynamic and magnetic measurements reveal that this compound is a realization of gapless QSL state down to at least 100 mK. *Ab initio* calculations find a strong magnetic exchange between Ir and Ni sublattices and in-plane antiferromagnetic coupling between the dimers, resulting in dynamically fluctuating magnetic moments.

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I. INTRODUCTION

Experimental realization and theoretical description of the highly entangled quantum spin-liquid (QSL) phase remain challenging topics of quantum many-body physics [1]. Over the past 15 years, several spin-1/2 systems with two-dimensional (2D) frustrated lattice have been reported as probable candidates with QSL behavior [2–6]. Since experimental reports of QSL with either spin (S) ≥ 1 [7,8] or 3D arrangement of spins [9–13] are very few, it can be easily anticipated that chances of having a QSL with both higher spin and 3D geometry is extremely low [14]. Many of the attempts to obtain spin-1 QSL have been focused on stabilizing Ni within various structural networks [7,8,14–17]. However, the magnetic behavior of these $S = 1$ systems at low temperature differs widely from each other, even in the compounds with similar structural geometry. For example, unlike the well-known 120° spin structure [18], as observed in $\text{A}_3\text{NiNb}_2\text{O}_9$ [16], $\text{Ba}_3\text{NiSb}_2\text{O}_9$ shows characteristic spin-liquid behavior [7,19,20], whereas NiGa_2S_4 hosts a spin-nematic phase [21]. The interaction of such Ni-based $S = 1$ triangular lattice with another magnetically active sublattice might result in an exotic magnetic phase in 3D materials. However, only very few 3D compounds with such feasibility exist [22–24].

Six-layered hexagonal ($6H$) perovskite $\text{A}_3\text{MM}'_2\text{O}_9$ [Fig. 1(a)] with magnetic M and M' ions constitutes a 3D spin system. Both MO_6 octahedral units and face-shared

$M'_2\text{O}_9$ dimers form a triangular lattice in a - b plane [Figs. 1(b) and 1(c)] and would become geometrically frustrated in the presence of antiferromagnetic (AFM) interaction. Moreover, the M - O - M' connectivity constitutes a buckled honeycomb lattice [Fig. 1(d)], which could host a Kitaev spin-liquid phase in case of spin-1/2 ions with strong spin-orbit coupling (SOC) [25,26]. In search of SOC-driven elusive nonmagnetic $J = 0$ state and excitonic magnetism in d^4 system, several $\text{Ba}_3\text{M}\text{Ir}_2\text{O}_9$ compounds with nonmagnetic M^{2+} have been investigated recently [27–30]. However, the comparable strength of SOC, noncubic crystal field, Hund's coupling, and superexchange interaction gives rise to a small but finite moment on the Ir sublattice. Moreover, interdimer hopping results in a spin-orbital liquid phase in $\text{Ba}_3\text{ZnIr}_2\text{O}_9$ [28]. Replacing the nonmagnetic Zn^{2+} by an isovalent magnetic ion such as Ni^{2+} should provide a unique opportunity to investigate the magnetic response of a triangular lattice with $S = 1$ in the presence of the interconnected Ir sublattice with fluctuating magnetic moments. If both Ni and Ir moments of $\text{Ba}_3\text{NiIr}_2\text{O}_9$ (BNIO) fluctuate dynamically, then it would offer a new route to realize 3D QSL by involving two different magnetic ions. Also, it would be a 3D QSL with a new type of structural network as compared to all existing examples with pyrochlore [12,14], hyperkagome [9], and hyper hyperkagome structure [10,13].

In this paper, we report on the electronic and magnetic behavior of BNIO. The phase purity and absence of any cationic site disorder have been demonstrated by powder x-ray diffraction (XRD) measurement. X-ray absorption spectroscopy (XAS) experiments have confirmed the desired $+2$

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FIG. 1. (a) Unit cell of $6H A_3MM'_2O_9$ without any disorder. (b), (c) The triangular lattice arrangement of M'_2O_9 dimers, MO_6 octahedra, respectively, in a - b plane. (d) M -O- M' connectivity forms buckled honeycomb lattice. A, M, and M' correspond to Ba, Ni, and Ir, respectively, for BNIO. Different magnetic exchange pathways (J_i) are also shown in (a)–(d). (e) Observed and refined powder XRD pattern of BNIO. (f) XAS spectrum of Ni $L_{3,2}$ -edge of BNIO along with NiO and $NdNiO_3$ for comparison. The XAS data for $NdNiO_3$ have been adapted from Ref. [31].

oxidation state of Ni. Persisting spin fluctuations down to 100 mK have been revealed by magnetization, specific heat, and muon spin-rotation (μ SR) measurements. We have also investigated electronic structure of BNIO by density functional theory (DFT) calculations including Hubbard U and SOC within the framework of the LSDA+ U (local spin density approximation + U) approach. We have found not only appreciable magnetic exchange between Ni and Ir-sublattice but also AFM coupling in the triangular sublattice of Ir. This geometrical frustration prohibits any long-range magnetic ordering and makes BNIO a rare example of 3D QSL involving $S = 1$.

II. METHODOLOGY

Stoichiometric amount of $BaCO_3$, NiO , and Ir metal powder was used as starting materials for the solid state synthesis of BNIO. The mixture was heated multiple times at $1175^\circ C$ with intermediate grindings until the desired phase was formed. Powder XRD was carried out using a laboratory-based Rigaku Smartlab diffractometer and also in the Indian beamline (BL-18B) at the Photon Factory, KEK, Japan. The diffraction pattern of the final phase was refined by the Rietveld method using FULLPROF [32].

XAS spectra of Ni $L_{3,2}$ -edges were recorded in bulk-sensitive total fluorescence yield mode in 4-ID-C beamline of Advanced Photon Source, USA. DC magnetic measurements

were carried out using a Quantum Design (QD) SQUID magnetometer. Heat capacity measurements at constant pressure (C_p) were done in a dilution refrigerator insert coupled with a 16T QD-PPMS system using relaxation calorimetry. μ SR experiments down to 60 mK were performed using pulsed muon beam at MuSR spectrometer of ISIS Neutron and Muon Source, UK. A dilution fridge was used to record μ SR data from 60 mK to 4 K and a cryostat was also used for temperatures above 1.5 K.

The DFT calculations have been performed in the LSDA+ U approach with and without including SOC by means of a full potential linearized muffin-tin orbital method (FP-LMTO) [33,34] as implemented in the RSPt code [35]. The Brillouin-zone (BZ) integration is carried out by using the thermal smearing method with $10 \times 10 \times 4$ k-mesh. For the charge density and potential angular decomposition inside the muffin-tin (MT) spheres, the value of maximum angular momentum was taken equal to $l_{max} = 8$. To describe the electron-electron correlation within LSDA+ U approach, we have taken $U = 6$ eV, $J = 0.8$ eV for Ni- d states and $U = 2$ eV, $J = 0.6$ eV for the Ir- d states. The set of the correlated orbitals located on Ni and Ir sites was obtained by projecting the electron density onto the corresponding MT sphere with a certain angular character (so-called “MT-heads” projection [36]).

After obtaining the self-consistent fully converged LSDA+ U +SOC calculations, the magnetic force theorem

FIG. 2. (a) Fitting of ρ by 3D VRH model for BNIO. Inset shows ρ vs T . (b) χ vs T on the left axis and $1/(\chi - \chi_0)$ along with fitting on the right axis. (c) M - H at 2 K.

[37,38] was used to extract the effective intersite magnetic-interaction parameters (J_{ij}). In this approach the magnetic system is mapped onto the Heisenberg Hamiltonian:

$$H = - \sum_{i \neq j} J_{ij} \vec{S}_i \cdot \vec{S}_j. \quad (1)$$

Further, J_{ij} are extracted in a linear-response manner via Green's function technique. A detailed discussion of the implementation of the magnetic force theorem in RSPt is provided in Ref. [39]. This method is considered to be one of the most accurate techniques for the estimation of exchange interactions and has also been successfully employed for many transition metal compounds [40].

III. RESULTS AND DISCUSSIONS

Members of the $A_3MM'_2O_9$ series can have site disorder between face-shared and corner-shared octahedra [41]. It is also well known that structural disorder often jeopardizes QSL behavior, resulting in magnetic order or spin-glass freezing [42]. All peaks of the powder XRD pattern of BNIO [Fig. 1(e)] can be indexed and refined with $6H$ structure having space group $P6_3/mmc$. The refinement also confirms that all corner-shared (face-shared) octahedral units are occupied by Ni (Ir) without any Ni-Ir site disorder. The structural parameters obtained from the refinement have been listed in the Supplemental Material [43]. The temperature-dependent XRD measurements down to 15 K also rules out any structural transition. Having confirmed that both Ni and Ir ions form triangular lattices in a - b plane without any disorder, we want to verify whether Ni has indeed $S = 1$ state. For this purpose, XAS measurements were carried out [31]. The comparison of Ni $L_{3,2}$ XAS line shape and energy position of BNIO, $Ni^{2+}O$ and $NdNi^{3+}O_3$ [Fig. 1(e)] testifies the desired +2 oxidation of Ni in the present case. The octahedral crystal field of Ni^{2+} (d^8 : t_{2g}^6, e_g^2) ensures $S = 1$ on Ni sublattice.

Electrical measurement demonstrates the insulating nature of the sample [inset in Fig. 2(a)], which can be fitted using Mott's variable range hopping (VRH) [44] model in 3D ($\rho = \rho_0 \exp(T_0/T)^{1/4}$) as shown in Fig. 2(a). We also note that the insulating behavior of $Ba_3ZnIr_2O_9$ is well described by VRH in 2D. This difference between two compounds is a manifestation of electron hopping paths along the Ni-O-Ir bonds. Our electronic structure calculations (see

Supplemental Material [43]) further demonstrate that the insulating state can be obtained only by considering both electron correlation and SOC, implying that BNIO is a SOC-driven Mott insulator [45].

The temperature-dependent field-cooled (FC) and zero-field cooled (ZFC) magnetic susceptibility does not differ from each other and also does not show any anomaly [Fig. 2(b)]. This strongly implies the absence of any long-range magnetic ordering and spin-glass behavior. We have fitted the data by a modified Cuire-Weiss law ($\chi = \chi_0 + \frac{C_W}{T - \theta_{CW}}$) where χ_0 , C_W , and θ_{CW} represent temperature-independent susceptibility contribution, Curie-Weiss constant, and Curie-Weiss temperature, respectively. The fitting, shown as a plot of $1/(\chi - \chi_0)$ vs T in the right axis of Fig. 2(b), results in $\theta_{CW} \sim -15$ K. Negative values of Curie-Weiss temperature signify net AFM interaction among the spins of BNIO. The relatively smaller value of θ_{CW} is related to the presence of multiple exchange pathways, which will be discussed in the latter part of this paper. The effective magnetic moment μ_{eff} ($=\sqrt{8C_W}$) is found to be $\sim 3.65 \mu_B$ from the fitting. Interestingly, the effective magnetic moment of a similar compound $Ba_3NiSb_2O_9$, with nonmagnetic Sb^{5+} , was reported to be around $3.54 \mu_B$ [7]. This gives an estimate of g factor ~ 2.5 , similar to other Ni^{2+} -based systems [46]. If we assume similar value for the present compound, the effective Ir moment turns out to be $0.9 \mu_B$ per dimer ($=\sqrt{\mu_{eff}^2 - \mu_{Ni}^2}$) i.e., $0.64 \mu_B$ /Ir. This is very similar to the Ir moment (0.5 – $0.6 \mu_B$) reported for $Ba_3MgIr_2O_9$ [29], though a nonmagnetic $J = 0$ state is expected for Ir^{5+} from a pure ionic picture. Thus, our analysis highlights both Ni^{2+} and Ir^{5+} participate in magnetism of BNIO compound. The estimated magnetic moments from our LSDA+ U +SOC calculations (shown in the Supplemental Material [43]) are also in good agreement with our experimental results. Figure 2(c) shows magnetization vs field (M - H) done at 2 K between ± 9 T. The absence of any hysteresis again confirms the absence of ferromagnetism (FM) and spin-glass freezing at 2 K. The presence of AFM interaction without any long-range magnetic ordering or spin-glass transition strongly indicates that BNIO is a favorable candidate of QSL.

In order to further investigate the magnetic nature of the sample, we have measured specific heat (C_p) from 100 mK to 200 K. C_p not only probes the presence/absence of any long-range magnetic ordering but also provides very crucial

FIG. 3. (a) C_p vs T curves at various fields. (b) Magnetic-specific heat (C_m) extracted by subtracting lattice contribution. (c) Low temperature part of C_m is plotted in a log-log plot. (d) Magnetic entropy for zero field.

information about the nature of low-energy excitations. The absence of any λ -anomaly [Fig. 3(a)] again confirms absence of long-range order and/or any structural transition down to 100 mK, consistent with the magnetic measurement and XRD results, respectively. For an insulating compound with magnetic spins, C_p consists of lattice-specific heat (C_{lat}) and magnetic-specific heat (C_m). In the absence of any analogous nonmagnetic compound, the contribution of C_{lat} has been evaluated by fitting C_p in the 30–200 K range by a Debye-Einstein equation with one Debye term and two Einstein terms (details are in the Supplemental Material [43]) and extrapolating the fitted curve down to 100 mK. A broad peak is observed around 7 K in C_m vs T plot [Fig. 3(a)]. We could not capture this feature by considering only Schottky anomaly, arising due to energy level splitting (see the Supplemental Material [43]). On the other hand, such feature is commonly observed in spin-liquid materials and thus could be considered as a signature of crossover from thermally disordered paramagnet to quantum disordered spin-liquid state [2,9,47,48]. The position of this broad peak shows negligible shifts with the application of magnetic field (shifts ~ 1 K for applied field of 12 T).

At low temperature, C_m follows power-law behavior $C_m = \gamma T^\alpha$ [Fig. 3(c)]. For zero field, the magnitude of coefficient γ is 45 mJ/mol K² and the exponent α is 1.0 ± 0.05 within a 0.1–0.6 K range. The value of γ is very similar to other gapless spin-liquid candidates like Ba₃CuSb₂O₉ (43.4 mJ/mol K²) [49], Ba₂YIrO₆ (44 mJ/mol K²) [50], Ba₃ZnIr₂O₉ (25.9 mJ/mol K²) [28], and Sr₂Cu(Te_{0.5}W_{0.5})O₆ (54.2 mJ/mol K²) [51]. Also, the linear T behavior with nonzero γ in an insulator comes due to gapless spinon excitations with a Fermi surface and has been reported in several organic and inorganic spin-liquid candidates [7,49,51–55]. Otherwise, any gapped excitation would result in an exponential dependence of C_m on T . The α becomes 2.6 ± 0.05 within 0.8–2.1 K. Interestingly,

FIG. 4. (a) Asymmetry vs time curves at various temperatures taken at zero magnetic field and fitted curve (solid line) using Eq. (2). (b) Variation of ν with temperature (thick curve is a guide to the eye). Inset shows variation of ν with applied LF at 100 mK.

the application of an external field destroys the linear T behavior of C_m . For $\mu_0 H = 4$ T, α becomes 2 for $0.15 \text{ K} \leq T \leq 0.50 \text{ K}$ and 2.9 for $0.5 \text{ K} \leq T \leq 2.4 \text{ K}$. We note that α is found to be between 2 and 3 for several spin-nematic phases [15,56–58]. Further studies are necessary to investigate the possibility of transition from spin-liquid to spin-nematic phase by the application of a magnetic field. The amount of released magnetic entropy (S_m) is evaluated by integrating C_m/T with respect to T and is shown in Fig. 3(d). For BNIO, the entropy saturates at 6.9 J/mol K for ZF measurement, which is only 75% of the total entropy expected for even a $S = 1$ system [$R \ln(2S + 1)$, where R is universal gas constant]. The retention of a large amount of entropy at low temperature is another signature of the spin-liquid nature of BNIO, which has been reported as well for many other QSL [7,49,51,52].

To have a further understanding of the magnetic behavior at low temperature, we have performed μ SR measurement, which is a very sensitive local probe to detect a weak magnetic field, even of the order of 0.1 Oe [59]. Figure 4(a) shows asymmetry vs time curves for ZF measurements at selected temperatures. Neither any oscillation nor the characteristic 1/3rd recovery of the asymmetry is observed down to 60 mK, strongly implying the absence of long-range magnetic ordering or spin freezing. For a system with two interacting spin

networks, the local magnetic field, felt by a muon at a stopping site, is contributed by both magnetic sublattices. In such cases, the muon relaxation function is generally described by a product of two response functions, representing local fields from two spin networks [60]. However, our such attempts considering different possible combinations of relaxation functions, including a spin-glass-like relaxation [60,61], did not provide a satisfactory fitting of the experimental observed data (see Supplemental Material [43]). This further supports the absence of spin-glass freezing in present case.

Interestingly, similar to the other hexagonal $\text{Ba}_3\text{M}\text{Ir}_2\text{O}_9$ [28,29], these asymmetry curves consist of one fast relaxing, one moderately relaxing, and one hardly relaxing components. We have fitted these curves using a combination of two dynamical relaxation functions with a common fluctuation rate ν and a static Kubo-Toyabe function (KT) [62],

$$A(t) = A_1 G(t, \Delta H_1, \nu) + A_2 G(t, \Delta H_2, \nu) + A_3 \text{KT}(t, \delta), \quad (2)$$

where A_1, A_2, A_3 are amplitudes. The static KT function, corresponding to the hardly relaxing component, accounts for the muons stopping at the silver sample holder as we find that the relaxation curve from the bare sample holder can also be described by a static KT function with similar δ . The dynamical relaxation, arising due to the presence of a field distribution (ΔH) with a fluctuation rate (ν) is represented by the Keren function $G(t, \Delta H, \nu)$ [63]. The presence of two dynamical relaxations implies two inequivalent muon stopping sites, which are likely to be related with the two types of crystallographically inequivalent oxygen in hexagonal $\text{Ba}_3\text{M}\text{Ir}_2\text{O}_9$ [28,29]. The asymmetry data over a large temperature range (60 mK–100 K) have been fitted by allowing ν to vary with T , and the extracted values of ν have been shown as a function of T in Fig. 4(b). The background contribution is different between measurements in dilution refrigerator and helium cryostat and has been kept fixed for our analysis within the corresponding temperature range (see Supplemental Material [43]). The inequality $\nu > \gamma \Delta H$ (γ = muon gyromagnetic ratio = $2\pi \times 135.5 \text{ Mrad s}^{-1} \text{ T}^{-1}$) holds for both relaxing components as $\gamma \Delta H_1 \sim 0.425 \text{ MHz}$ and $\gamma \Delta H_2 \sim 0.09 \text{ MHz}$ for the lowest temperature of our measurement (60 mK). This justifies the use of dynamical relaxation functions and establishes spin-liquid nature of BNIO. We note that the value of ν ($\sim 4 \text{ MHz}$) at low temperature for BNIO is one order of magnitude smaller than $\text{Ba}_3\text{ZnIr}_2\text{O}_9$ [28] and is likely to be related with the involvement of large spins on the Ni sublattice.

μ -SR spectra, recorded at 100 mK in presence of an applied longitudinal field (LF), have further corroborated QSL nature of BNIO. In case of relaxation arising from a static internal field distribution with width ΔH_i , an applied LF $\sim 5\text{--}10\Delta H_i$ would completely suppress the relaxation. From the analysis of ZF μ SR data, we found $\Delta H_1 \sim 5 \text{ Gauss}$ and $\Delta H_2 \sim 1 \text{ Gauss}$. No such decoupling is observed in the present case in measurement up to 200 Gauss [see inset of Fig. 4(b) and Supplemental Material [43]], establishing the dynamic nature of spins in BNIO down to at least 100 mK.

To understand the underlying mechanism of the observed QSL state, we estimated the interatomic magnetic exchange interactions from the converged LSDA+ U +SOC calculations

TABLE I. Exchange couplings obtained from *ab initio* calculations. Exchange pathways have been shown in Fig. 1. AFM and FM refer to antiferromagnetic and ferromagnetic interaction, respectively.

Exchange (J_i)	Interacting pair	Number of neighbor (z_i)	Magnitude (meV)	type	$ z_i J_i / J_1 $
J_1	Ir-Ir	1	−8.91	AFM	1
J_2	Ir-Ni	3	0.96	FM	0.32
J_3	Ir-Ir	3	0.10	FM	0.03
J_4	Ir-Ir	6	−0.17	AFM	0.11
J_5	Ni-Ni	6	0.09	FM	0.06

using the formalism of Ref. [39]. As shown in Table I, the strongest interaction is AFM, which is between the Ir ions of the structural dimer. The strong Ir-Ni interaction further testifies to the 3D nature of BNIO. Most importantly, Ir-Ir exchange in the *a-b* plane (J_4) is found to be AFM, resulting in in-plane magnetic frustration and explains the origin of the QSL behavior of the present system. However, the presence of strong Ir-Ni and Ni-Ni FM exchange reduces the net AFM exchange of this system, resulting in a relatively lower value of negative θ_{CW} . We further note that the FM Ni-Ni exchange has been observed also in the AFM phase of analogous compound $\text{Ba}_3\text{NiRu}_2\text{O}_9$ [23].

IV. CONCLUSION

To summarize, our detailed measurements reveal that $6H$ BNIO containing $S = 1$ hosts a gapless spin-liquid phase below 2 K. The involvement of Ir^{5+} and Ni^{2+} in the magnetic properties of BNIO is revealed by dc magnetic measurements, μ SR experiments, and electronic structure calculation. The AFM interaction between Ir_2O_9 dimers in *a-b* plane facilitates geometrical frustration-driven QSL phase of BNIO. Our work provides a new route to realize 3D QSL with large spins involving two different magnetic ions.

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