Spin Liquid Behavior in the Disordered Double Perovskite BaTi$_{1/2}$Mn$_{1/2}$O$_3$

M.R. Cantarino$^1$, R.P. Amaral$^2$, R.S. Freitas$^3$, J.C.R. Araújo$^2$, R. Lora-Serrano$^2$, H. Luetkens$^3$, C. Baines$^3$, S. Bräuning$^4$, V. Grinenko$^4$, R. Sarkar$^4$, H.H. Klauss$^4$, E. C. Andrade$^5$, F. A. Garcia$^1$

$^1$IFUSP, Univ. de São Paulo, 05508-090, São Paulo-SP, Brazil
$^2$Univ. Fed. de Uberlândia, Instituto de Física, 38400-902, Uberlândia-MG, Brazil
$^3$Laboratory for Muon Spin Spectroscopy, Paul Scherrer Institute, CH-5232 Villigen PSI, Switzerland
$^4$Institute for Solid State and Material Physics, TU Dresden, D-01069 Dresden, Germany and
$^5$Instituto de Física de São Carlos, Universidade de São Paulo, C.P. 369, São Carlos, SP, 13560-970, Brazil

We investigate the low-temperature ($T$) magnetic properties of the disordered double perovskite BaTi$_{1/2}$Mn$_{1/2}$O$_3$, where the magnetic $S = 3/2$ Mn$^{4+}$ cations can either form magnetic trimers or dimers or remain as orphan spins. The heat capacity and magnetic susceptibility are measured for temperatures down to $T = 0.1$ K, and magnetic fields up to 10 T. The data display no evidence for a phase transition to a magnetically ordered phase but indicate the formation of a correlated spin state. The low-temperature spin dynamics of this state is then explored by $\mu$SR experiments. The zero field $\mu^+$ relaxation rate data display no features due to magnetic ordering down to $T = 19$ mK and longitudinal field experiments support as well that dynamic magnetism persists at low--$T$. Thus, our data provide evidence BaTi$_{1/2}$Mn$_{1/2}$O$_3$ is a candidate to host a spin liquid ground state.

**Introduction:** Transition metal ($M$) oxides are forever the source of intriguing new physics in the field of correlated electron systems, including a large number of complex magnetic systems [1]. Complexity emerges from the magnetic interaction between the spins at the $M$ sites, which takes place by means of a superexchange interaction [2] that will usually drive the system to a magnetic ordered state [3]. In some materials, however, dimensionality, lattice geometry or the symmetry of the interactions may hinder the appearance of long range order [4–8]. In these cases, at sufficient low temperatures ($T$), the system may be driven to some exotic ground state, such as a quantum spin liquid (SL) ground state. A SL state is a disordered quantum magnetic state wherein the spins are entangled in a highly correlated and dynamical state of matter [9–11].

The first task to experimentally verify the formation of a SL state is to provide evidence for the lack of phase transitions down to the lowest temperatures. It is paramount, as well, to present evidence that a collective spin state is formed at low--$T$, most striking by characterizing continuous magnetic excitations [12–14] or the spin relaxation rate regime. For the later purpose, muon spin relaxation ($\mu$SR) is a particular appropriate technique [15–18].

In the disordered double perovskite BaTi$_{1/2}$Mn$_{1/2}$O$_3$, $S = 3/2$ spins due to Mn$^{4+}$ cations pair up to form magnetic dimers in a singlet state, coexisting with orphan spins [19] ($S = 3/2$) and magnetic trimers [20]. The formation of dimers and trimers are dictated by large energy scales ($\approx 100–175$ K) and the effective low--$T$ degrees of freedom involve orphan spins and trimers, organized in bilayers of triangular lattices, with competing antiferromagnetic exchange interactions including both inter and intra layer energy scales. In this paper, we propose that this novel configuration paves the way for a SL ground state in our system, comprised of coupled $S = 3/2$ (orphans) and effective $S = 1/2$ spins (trimers). We present and discuss low--$T$ heat capacity and susceptibility data which show no sign of long-range order, but which indicate a highly correlated magnetic state. Subsequently, we explore the spin dynamics of our system by $\mu$SR, and we show that dynamic magnetism persists down to the lowest temperatures (70 K) achieved in our experiments.

**Methods:** Heat capacity measurements were performed to temperatures down to 0.1 K and magnetic fields up to 9 T, employing a Quantum Design PPMS using a dilution refrigerator. Susceptibility ($\chi(T)$) measurements were performed for temperatures down to 0.5 K employing a Quantum Design Magnetometer ($2 – 300$ K) and a Vibrating Sample Magnetometer (VSM) in a $^3$He cryostat. Isothermal magnetization ($M(H)$) were measured for $T ≥ 0.6$ K for magnetic fields up to 10 T using the VSM.

$\mu$SR measurements have been carried out at the $\pi$M3 beam line at the GPS and LTF spectrometers of the Swiss Muon Source at the Paul Scherrer Institute (PSI) in Villigen. The measurements were performed in the $T$ interval 0.019 < $T$ < 10 K (LTF) and 1.5 < $T$ < 200 K (GPS) [21] in zero magnetic field (ZF) and in longitudinal applied magnetic fields (LF) with respect to the initial muon spin polarization up to 0.05 T. To improve the thermal contact, the samples in the experiments at the LTF spectrometer were glued on a Ag plate. This gives rise to a time and temperature independent background due to muons that stopped in the Ag plate. The $\mu$SR time spectra were analyzed using the free software package MUSRFIT [22].

**Structure, magnetism and heat capacity:** The BaTi$_{1/2}$Mn$_{1/2}$O$_3$ structure is presented in Fig. 1(a). It was originally explored by Keith et al [23] and subsequent papers [20, 24]. The structure possesses 3 transition metal sites, termed $M(1)$, $M(2)$ and $M(3)$. Mn cations are found at the $M(1)$ and $M(2)$ sites. The $M(1)$ sites are occupied exclusively by Mn atoms whereas the occupation of the $M(2)$ sites is mixed. Half the Mn...
Figure 1. (a) Structural model of BaTi$_{1/2}$Mn$_{1/2}$O$_3$ with a 12R-type perovskite structure. Barium (Ba(1) and Ba(2)), oxygen (O(1) and O(2)) and transition metal (M(1), M(2) and M(3)) sites are indicated. (b) Detail of the structural trimer indicating the $J_1$ and $J_2$ exchange constants. (c) Model of the proposed emerging magnetic lattice at low $T$.

...will form magnetic trimers, 2/6 form magnetic dimers and 1/6 are orphans. The coupling of magnetic dimers and trimers are described by two strong exchange constants $J_1$ and $J_2$ (Fig. 1(b)) [20].

As a function of $T$, the dimer contribution to magnetism is exponentially suppressed and we can safely assume that at low–$T$ it is dominated by orphan spins and magnetic trimers. Focusing on the plane formed by the M(1) sites, one may propose the following emerging 2D structure for the magnetic lattice represented in Fig. 1(c): bilayers of triangular lattices (lattice constant $a = 5.69$ Å) with a Mn atom (or trimer) at each site in a AB stacking (the lattice sites in the upper layer are directly over the centers of triangles of the bottom layer and vice-versa). Each bilayer lies between layers of magnetic dimers, thus being magnetically isolated from each other.

In panel (a) of Fig. 2 we present heat capacity measurements, $C_p$, as a function of $T$ ($0.2 < T < 100$ K) for distinct values of $H$. The data give no evidence for a phase transition down to $T = 0.2$ K , presenting only a broad anomaly peaking at about 3 K for $H = 0$. The anomaly is clearly $H$ dependent thus of magnetic nature. We shall interpret this anomaly as a crossover to our putative SL state. Below and about $T \lesssim 0.2$ K the data present an upturn at low –$T$ that could be interpreted as the tail of a transition at further lower temperatures.

This upturn, however, is actually due to the Mn nuclear contribution to the heat capacity. In the inset on the same figure, we compare the data for $H = 0$ with the MnSi heat capacity in this low–$T$ region ($T < 0.2$ K). Following the subtraction of the MnSi heat capacity (as a way to estimate the nuclear contribution) it is relatively safe to assert that no phase transition is observed down to 0.1 K.

In panel (b), $\chi(T)$ measurements are presented in the interval $0.6 < T < 330$ K. To describe the data in the range $T > 5.5$ K, which is above the crossover region, we refer to our model (see supplemental material Ref. [25]) including magnetic dimers and trimers plus orphan spins. The obtained parameters associated to dimers and trimers are $J_1 = 175(5)$ K and $J_2 = 0.58(5)J_1$. Orphan spins are modeled by a Curie-Weiss type susceptibility, and the obtained parameters are $\theta_{orp} = -7.3(3)$ K and $C_{orp} = 0.12(1)$ emu.K/mol (f.u.). We call attention that $C_{orp} = 0.12(1)$ emu.K/mol (f.u.) must be compared with $C \approx 0.15$ emu.K/mol (f.u.) expected for $1/12$ mols of Mn.

In Fig. 2(c) isothermal, $T = 0.6$ K, $M(H)$ measurements, for $H$ up to 10 T are presented. The absence of hysteresis is noteworthy and is another piece of evidence that the system is not in a magnetic ordered phase.

A SL manifests clearly in the behavior of the magnetic specific heat, $C_{mag}$. In general, the measured heat capacity, $C_p$, will include two distinct contributions: $C_p(T) = C_{lattice}(T) + C_{mag}(T)$. Following the subtraction of the phonon contribution ($C_{lattice}$, [25]), $C_{mag}$ is presented in panel (a) of Fig. 3 for $H$ up to 9 T. Inspecting the broad anomalies, we observe that the peaks displace to higher temperatures (from $T \approx 3$ – 7 K) with increasing field. To characterize this putative SL state, we focus on the low temperature region ($0.2 \leq T \leq 1.0$ K) and investigate the excitations of the SL phase. It is adopted that $C_{mag}(T)$ will in general follow a power law in the low–$T$ region and the data are fitted to the expression $C_{mag}(T) = \gamma(H)T^{\alpha(H)}$. The dashed lines are representative ($H = 0$ T and $H = 9$ T) fittings. The resulting parameters, $\gamma(H)$ and $\alpha(H)$, are shown Fig. 3(b). Within error bars, $\alpha(H)$ is nearly constant assuming a
value of about $\approx 1.4 - 1.5$, suggesting gapless excitations of the SL state. Moreover, $C_{\text{mag}}/T$ do not diverge as $T \to 0$, meaning that our system is away from quantum criticality [26]. The value of $\gamma(H)$ decreases with increasing field from $\gamma \approx 0.45$ to $\gamma \approx 0.25$ J/mol(Mn)K$^\alpha$ at $H = 9$ T, indicating quenching of the magnetic entropy as a function of the field, albeit there are no free spins in the system. These values are relatively large when compared to other SL candidates [27].

The nature of the zero field $C_{\text{mag}}$, in particular, is key to estimate the total entropy recovered in the ground state and to reveal the total fraction of spins that are part of the proposed correlated state. In Fig. 3(c), we show the heat capacity data and the magnetic entropy ($\Delta S(T)$) for $H = 0$ in the interval $0.1 \leq T \leq 20$ K. The total entropy recovered by the system amounts to $1.95(5)$ J/K.mol(Mn). This entropy may be only due to orphans and trimers, since the dimer entropy is recovered at much higher temperature [25]. For a fraction $f_{3/2}$ of $S = 3/2$ spins, the total entropy recovered by the system is $f_{3/2} \times R \ln 4$ per mol of $S = 3/2$ spins. In the present case, $f_{3/2} = 1/6$, thus the total entropy due to orphans is expected to be $\approx 1.92$ J/K.mol(Mn), corresponding closely to the experimental result. This is surprising since there is still the entropy due to the effective $S = 1/2$ spins of the magnetic trimers left behind in the system. The trimers, however, are not in a simple paramagnetic state for such state would imply: (i) sizable Schottky anomalies in the field dependent heat capacity measurements, and (ii) a Curie-like response in the magnetic susceptibility, both which are not observed [25]. In overall, if we consider the total entropy due to trimers and orphans in the system, we may assert that we recover a total of $\approx 2/3$ of the expected system entropy.

$\mu$SR ZF and LF experiments: we now turn our attention to our $\mu$SR experiments [16]. In Fig. 4(a)-(d) we present ZF $\mu$SR data measured for temperatures down to $T = 0.019$ K. Down to the lowest temperatures, the spectra (Figs. 4(a)-(b)) can be described quite well by an exponential decay, and the data do not present the characteristic damped oscillations of a magnetic ordered phase [16]. Fig 4(a) shows the temperature interval for which the spectra change the most ($1.5 < T < 10$ K), characterizing a crossover behavior in this region. Fig 4(b) display the low temperature spectra, which can be almost described by a single fitting below $T < 1.5$ K. The theoretical curves represent the best fitting to a stretched exponential which describe the asymmetry function $A(t) = A_0 \exp(-\lambda t)^{\beta} + B$, where $A_0$ is the starting asymmetry, $B$ describes the constant background mostly due to muons that did not stop in the sample and $\lambda$ and $\beta$ are, respectively the relaxation rate and the stretching exponent.

The resulting fitting parameters $\lambda$ and $\beta$ are shown in Figs 4(c)-(d). For $T > 10$ K, $\lambda$ is nearly temperature independent, as typical for simple paramagnets. In the $T-$region $1.5 < T < 10$ K, $\lambda$ goes through a steep increase from $\approx 0.7 \mu$s$^{-1}$ up to a constant value $\approx 1.2 \mu$s$^{-1}$ for $T < 1.5$ K, characteristic of a crossover behavior, reminiscent of most SL ground states [15, 17, 18]. The $\beta$ coefficient do also display a crossover behavior in this same $T-$region. Its value decreases from $\approx 1$ at high $T$ to a constant value close to 0.5 for $T < 1.5$ K. This value is well above 1/3 that would be expected for glassy dynam-

---

**Figure 2.** (a) Heat capacity ($C_p$) measurements as a function of $T$ and applied field $H$. The inset shows the Mn nuclear contribution to the heat capacity. (b) Susceptibility ($\chi(T)$) measurements as a function of $T$ ($0.5 \leq T \leq 330$ K). The inset shows $\chi(T)$ data for $T < 2$ K. The fitting (thick line) is discussed in Ref. [25]. (c) Isothermal ($T = 0.6$ K) magnetization measurements as a function of $H$ ($M(H)$).

**Figure 3.** (a) Magnetic specific heat, $C_{\text{mag}}(T)$, obtained after the subtraction of the lattice contribution. The dashed lines are representative fittings ($H = 0$ and $H = 9$ T) to $C_{\text{mag}}(T) = \gamma(H)T^{\alpha}(H)$ . (b) Full set of field dependent parameters $\gamma(H)$ and $\alpha(H)$ obtained from this fitting. (c) Zero field magnetic specific heat data and the total magnetic entropy $\Delta S(T)$. 
ics, indicating the absence of static local fields [16]. It is noteworthy that the crossover region detected by the μSR corresponds closely to the region where the broad peak is observed for the heat capacity measurements. Our data illustrates a good qualitative agreement between macroscopic and microscopic measurements.

We have as well performed LF measurements at $T = 0.1 \text{ K}$ and the results are presented in Fig 4(e). The data is compared with the expected results from the dynamical Kubo-Toyabe (DKT) theory. The change in the spectra as a function of field (from 0 to 0.05 T) is much less dramatic than the expected from the DKT theory. This is a compelling piece of evidence for dynamic magnetism at temperatures down to $T = 0.1 \text{ K}$. Following Refs. [15, 17], the spin fluctuation rates for temperatures above and below the crossover can be estimated [25]. The results are $\nu_{T>0.1 \text{ K}} = 7.4(1) \times 10^{10} \text{ Hz}$ and $\nu_{T<0.1 \text{ K}} = 3.7(6) \times 10^{6} \text{ Hz}$, suggesting, without symmetry breaking, the onset of long-time spin correlations in the system for $T < 1.5 \text{ K}$. In turn, it can be interpreted as the formation of an entangled spin state in the system.

The nature of the spin liquid. The experimental results are compatible with a gapless SL. Because the magnetic susceptibility saturates at low-$T$, a strong candidate would be an SL with a spinon Fermi-surface. However, for this system, we expect $C_{\text{mag}} \sim T^{2/3}$ [17, 29] for zero field, unlike the $T^{3/2}$ we observe. Another possibility would be an $U(1)$ Dirac spin-liquid [30–32]. Here, one expects $C_{\text{mag}} \sim T^2$ at zero fields and $C_{\text{mag}} \sim T$ at low-fields, and that $C_{\text{mag}}$ should increase with the field, which we also do not observe. An intriguing alternative possibility would be that that orphan spins form an algebraic spin liquid and that the trimers are Kondo screened by the spinons with a Kondo temperature $T_K \lesssim 1 \text{ K}$ [33, 34], which is qualitatively consistent with our measurements [35]. Naturally, we would then expect a hybridization gap to appear at lower temperatures. A major difficulty with this scenario is that recent theoretical investigations [36–38] show that a parameter fine-tuning is required to observe an SL in the triangular lattice, even for $S = 1/2$, given the reduced volume of the phase diagram it occupies.

A similar drawback is recently under debate in YbMgGaO$_4$, where the observed SL behavior is not captured by the minimal theoretical model [13, 17, 27, 28]. One possible scenario to understand the reported experimental behavior is to take into account the presence of disorder in the system [39], which may have non-trivial effects, even leading to the destruction of long-range magnetic order [40–42]. Since the μSR results for YbMgGaO$_4$ are qualitatively similar to ours [17], we cannot exclude the role of disorder in understanding the behavior of BaTi$_{1/2}$Mn$_{1/2}$O$_3$.

Ultimately, we can only account, experimentally, for $2/3$ of the total entropy of the system, suggesting that the observed SL state includes some residual entropy, as observed recently in other SL candidates [43, 44]. It could be that the measured SL state is not the true ground state, but only a crossover regime. If this is true, the coupling between the adjacent layers of $S = 1/2$ and $S = 3/2$ would lead the system to order, most likely in a ferrimagnetic state [45] at a temperature which is much too low to be detected by our experimental probes.

Conclusion. We have performed macroscopic and microscopic experiments in the disordered double perovskite BaTi$_{1/2}$Mn$_{1/2}$O$_3$. This complex material displays a rich magnetic behavior with the physics at high temperatures dominated by the presence of trimers, dimers, and orphan spins [20]. At lower temperatures, the effective magnetic degrees of freedom, composed by orphan spins and trimers, are found to be correlated but no phase transition is detected down to $T = 0.1 \text{ K}$, de-

![Figure 4](image_url)
spite the effective exchange couplings being of the order of 10 K. µSR measurements then show substantial evidence for dynamic magnetism down to $T = 0.019$ K, a behavior expected for a spin liquid system. The proper characterization of this novel state requires further theoretical and experimental efforts.

ACKNOWLEDGMENTS

MRC acknowledges CNPq grant No.131117/2017-3 for financial support. RSF acknowledges FAPESP grant No.2015/16191-5 and CNPq grant No.306614/2015-4. RLS acknowledges FAPEMIG-MG (APQ-02256-12) and CAPES Foundation (Brazil) for grant EST-SENIOR-88881.119768/2016-01. Author VG is supported by GR 4667. RS and HHK are partially supported by DFG SFB 1143 for the project C02. ECA acknowledges FAPESP Grant No. 2013/0681-8 and CNPq Grant No. 302065/2016-4.

[1] E. Dagotto, Science 309, 257 (2005).
[2] J. B. Goodenough, *Magnetism And The Chemical Bond* (John Wiley And Sons, 1963).
[3] R. M. White, *Quantum theory of magnetism magnetic properties of materials* (Springer, Berlin, 2007).
[4] P. W. Anderson, Mater. Res. Bull. 8, 153 (1973).
[5] N. Read and S. Sachdev, Phys. Rev. Lett. 62, 1694 (1989).
[6] A. Kitaev, Annals of Physics January Special Issue, 321, 2 (2006).
[7] J. S. Helton, K. Matan, M. P. Shores, E. A. Nytko, B. M. Bartlett, Y. Yoshida, Y. Takano, A. Suslov, Y. Qiu, J.-H. Chung, D. G. Nocera, and Y. S. Lee, Physical Review Letters 98, 107204 (2007).
[8] M. Mourigal, M. Enderle, A. Klöpperpieper, J.-S. Caux, A. Stunault, and H. M. Ronnow, Nature Phys. 9, 435 (2013).
[9] L. Savary and L. Balents, Rep. Prog. Phys. 80, 016502 (2017).
[10] Y. Zhou, K. Kanoda, and T.-K. Ng, Reviews of Modern Physics 89, 025003 (2017).
[11] T.-H. Han, J. S. Helton, S. Chu, D. G. Nocera, J. A. Rodriguez-Rivera, C. Broholm, and Y. S. Lee, Nature 492, 406 (2012).
[12] J. A. M. Paddison, M. Daum, Z. Dun, G. Ehlers, Y. Liu, M. B. Stone, H. Zhou, and M. Mourigal, Nature Physics 13, 117 (2017).
[13] C. Balz, B. Luke, J. Reuther, H. Luetkens, R. Schönenmann, T. Herrmannsdörfer, Y. Singh, A. T. M. Nazmul Islam, E. M. Wheeler, J. A. Rodriguez-Rivera, T. Guidi, G. G. Simeoni, C. Baines, and H. Ryll, Nature Physics 12, 942 (2016).
[14] Y. J. Uemura, A. Keren, K. Kojima, L. P. Le, G. M. Luke, W. D. Wu, Y. Ajiro, T. Asano, Y. Kuriyama, M. Mekata, H. Kikuchi, and K. Kakurai, Physical Review Letters 73, 3306 (1994).
[15] S. J. Blundell, Contemporary Physics 40, 175 (1999).
[16] Y. Li, D. Adroja, P. K. Biswas, P. J. Baker, Q. Zhang, J. Liu, A. A. Tsirlin, P. Gegenwart, and Q. Zhang, Physical Review Letters 117, 097201 (2016).
[17] P. Khuntia, F. Bert, P. Mendels, B. Koteswararao, A. V. Mahajan, M. Baenitz, F. C. Chou, C. Baines, A. Amato, and Y. Furukawa, Physical Review Letters 116, 107203 (2016).
[18] P. Schiffer and I. Daruka, Physical Review B 56, 13712 (1997).
[19] F. A. Garcia, U. F. Kaneko, E. Granado, J. Sichelschmidt, M. Hözel, J. G. S. Duque, C. A. J. Nunes, R. P. Amaral, P. Marques-Ferreira, and R. Lora-Serrano, Physical Review B 91, 224416 (2015).
[20] A. Amato, H. Luetkens, K. Sedlak, A. Stoykov, R. Scheuermann, M. Elender, A. Raselli, and D. Graf, Review of Scientific Instruments 88, 093301 (2017).
[21] A. Suter and B. M. Wojek, Physics Procedia 12th International Conference on Muon Spin Rotation, Relaxation and Resonance (IESR2011), 30, 69 (2012).
[22] G. M. Keith, C. A. Kirk, K. Sarma, N. M. Alford, E. J. Cussen, M. J. Rosseinsky, and D. C. Sinclair, Chemistry of Materials 16, 2007 (2004).
[23] L. Miranda, A. Feteira, D. C. Sinclair, K. Boulahya, M. Hernando, J. Ramirez, A. Varela, J. M. Gonzalez-Calbet, and M. Parras, Chemistry of Materials 21, 1731 (2009).
[24] M. R. Cantarino, R. P. Amaral, R. S. Freitas, J. C. R. Araújo, R. Lora-Serrano, H. Luetkens, C. Baines, S. Bräuninger, V. Grinenko, R. Sarkar, H. H. Klaus, E. C. Andrade, and F. A. Garcia, Supplemental Material (2018).
[25] Y. Singh, Y. Tokiwa, J. Dong, and P. Gegenwart, Physical Review B 88, 220413 (2013).
[26] Y. Li, H. Liao, Z. Zhang, S. Li, F. Jin, L. Ling, L. Zhang, Y. Zou, L. Pi, Z. Yang, J. Wang, Z. Wu, and Q. Zhang, Scientific Reports 5, 16419 (2015).
[27] Y. Li, G. Chen, W. Tong, L. Pi, J. Liu, Z. Yang, X. Wang, and Q. Zhang, Physical Review Letters 115, 167203 (2015).
[28] O. I. Motrunich, Phys. Rev. B 72, 045105 (2005).
[29] Y. Ran, M. Hermle, P. A. Lee, and X.-G. Wen, Phys. Rev. Lett. 98, 117205 (2007).
[30] S. Ryu, O. I. Motrunich, J. Alicea, and M. P. A. Fisher, Phys. Rev. B 75, 184406 (2007).
[31] Y.-C. He, M. P. Zaletel, M. Oshikawa, and F. Pollmann, Phys. Rev. X 4, 031020 (2017).
[32] Y. Li, H. Liao, Z. Zhang, S. Li, F. Jin, L. Ling, L. Zhang, Y. Zou, L. Pi, Z. Yang, J. Wang, Z. Wu, and Q. Zhang, Scientific Reports 5, 16419 (2015).
[33] S. Florens, L. Fritz, and M. Vojta, Phys. Rev. B 96, 036601 (2006).
[34] M. Vojta, A. K. Mitchell, and F. Zschocke, Phys. Rev. Lett. 117, 037202 (2016).
[35] A. C. Hewson, *The Kondo Problem to Heavy Fermions*, 1st ed. (Cambridge University Press, Cambridge, 1993).
[36] Z. Zhu and S. R. White, Phys. Rev. B 92, 041105 (2015).
[37] W.-J. Hu, S.-S. Gong, W. Zhu, and D. N. Sheng, Phys.
Rev. B 92, 140403 (2015).

[38] Z. Zhu, P. A. Maksimov, S. R. White, and A. L. Chernyshhev, ArXiv e-prints (2018), arXiv:1801.01130.

[39] Y. Li, D. Adroja, R. I. Bewley, D. Voneshen, A. A. Tsirlin, P. Gegenwart, and Q. Zhang, Physical Review Letters 118, 107202 (2017).

[40] Z. Zhu, P. A. Maksimov, S. R. White, and A. L. Chernyshhev, Phys. Rev. Lett. 119, 157201 (2017).

[41] E. C. Andrade, J. A. Hoyos, S. Rachel, and M. Vojta, ArXiv e-prints (2017), arXiv:1710.06658.

[42] E. Parker and L. Balents, arXiv:1801.06941 (2018).

[43] R. Kumar, D. Sheptyakov, P. Khuntia, K. Rolfs, P. G. Freeman, H. M. Rønnow, T. Dey, M. Baenitz, and A. V. Mahajan, Physical Review B 94, 174410 (2016).

[44] R. Kumar, P. Khuntia, D. Sheptyakov, P. G. Freeman, H. M. Rønnow, B. Koteswararao, M. Baenitz, M. Jeong, and A. V. Mahajan, Physical Review B 92, 180411 (2015).

[45] E. Lieb and D. Mattis, J. Math. Phys. 3, 749 (1962), https://doi.org/10.1063/1.1724276.
Here we present in detail some aspects of the data treatment, complementary data and some explanatory notes to give support to our discussion in the main text. In turn, we give details about 1) analysis of $\chi(T)$ (that can be found on our previous paper Ref. [1]); 2a) extraction of $C_{\text{mag}}$; 2c) Fittings of $C_{\text{mag}}$ and $2c$) analysis of the Schottky anomalies; 3) Dynamic spin susceptibility analysis (to determine the spin relaxation rates discussed in the main text).
I. SUSCEPTIBILITY

The detailed analysis of the high temperature susceptibility ($\chi(T)$) was the subject of a previous paper by some of the authors [1]. Here, we give a fast account of this previous discussion in order to set the context. The magnetic properties of the paramagnetic state is rooted in the structural model. In Reference to Fig.1(a) in the main text, the BaTi$_{1/2}$Mn$_{1/2}$O$_3$ unit cell contains 3 $M(1)$ and $M(3)$ sites and 6 $M(2)$ sites. All sites occupied by Mn atoms are inside the structural trimers ($M(1)$ and $M(2)$ sites). The $M(1)$ and $M(2)$ sites are inside face sharing oxygen octahedra, giving rise to a large multiplicity of exchange paths. As a consequence, one may expect the exchange coupling between the Mn cations to be large. We name $J_1$ the first neighbor super-exchange constant and $J_2$ the second neighbour super-super-exchange (indicated Fig.1(b) of the main text). These are effective constants taking into account all multiplicity of the exchange paths.

There are 3 possible configurations for the occupancy of the structural trimers: 3 Mn cations, 2 Mn cations plus 1 Ti cation and 1 Mn cation plus 2 Ti cations. Each of these configurations will, respectively, give the following contributions to $\chi(T)$: magnetic trimers ($\chi(T)_{\text{trim}}$), magnetic dimers $\chi(T)_{\text{dim}}$ and orphan spins $\chi(T)_{\text{orp}}$. By inspection, we expect that 3/6 of Mn will form trimers, 2/6 will form dimers and 1/6 will be orphans.

The dimer contribution, can be deduced from the following Hamiltonian:

$$\mathcal{H}_{\text{dimer}} = J_1 S_1 S_2$$

The trimer contribution, an be deduced from the following Hamiltonian:

$$\mathcal{H}_{\text{trim}} = J_1 S_1 S_2 + J_1 S_2 S_3 + J_2 S_1 S_3$$

As for the orphan spins, its contribution are modeled by a Curie-Weiss type susceptibility:

$$\chi(T) = \frac{C_{\text{orp}}}{T - \theta_{\text{orp}}} + \chi_0$$

The obtained parameters are: $J_1 = 175(5)$ K, $J_2 = 0.58 J_1$, $\theta_{\text{orp}} = -7.3(3)$ K and $C_{\text{orp}} = 0.12(1)$ emu.K/mol (f.u.). The numbers are slightly different than previously [1] mostly for three reasons: (1) the restricted temperature interval ($T > 5.5$ K); (2) new, and improved, sample batch; (3) change in the counting of the Mn in each state. We call attention that $C_{\text{orp}} = 0.12(1)$ emu.K/mol (f.u.) must be compared with $C \approx 0.15$ emu.K/mol (f.u.) expected for 1/12 mols of Mn $S = 3/2$ spins per formula unit of BaTi$_{1/2}$Mn$_{1/2}$O$_3$, which is a very good agreement, specially taking into account the complexity of the system. As for $\theta = -7.3(3)$ K, since there is no phase transition down to 100 mk (see the inset of Fig.2a of the main text), one can estimate a lower bound for the frustration parameter as $f \approx 7.3/0.1 = 73$.

For $J_1 = 175(5)$ K, $J_2 = 0.58 J_1$, the trimer ground state is an effective $S = 1/2$ spin with the first excited state lying $\approx 30$ K above the ground state. Therefore, as a way to estimate the orphan-trimer interaction, we model the system in a mean field approximation [2] considering coupled $S = 3/2$ and $S = 1/2$ spins plus a dimer contribution. The resulting effective energy scale is $\theta_{\text{orp-tri}} = -8.5(5)$ K. The resulting Curie constant is $C_{\text{orp-tri}} = 0.19(1)$ emu.K/mol (f.u.) which compares well with the expected $\approx 0.18$ emu.K/mol (f.u.).

II. HEAT CAPACITY

A. Subtraction of the phonon contribution

The heat capacity data is presented in Fig. S1(a). Our main objective is to extract the magnetic heat capacity in the low temperature region (to be understood as $0.2 \leq T \leq 20$ K) to characterize the excitations of the proposed spin liquid phase. The total heat capacity includes two contributions:

$$C_p = C_{\text{lattice}} + C_{\text{mag}}$$

where $C_{\text{lattice}}$ is the lattice specific heat and $C_{\text{mag}}$ is the magnetic specific heat. First, we proceed to subtract the lattice contribution. In the absence of a suitable non magnetic reference compound, we will proceed as follows: i) first, we fit the $T \geq 25$ K (above which the heat capacity is not $H^-$ dependent and thus is dominated by phonons)
heat capacity data obtained for $H = 0$ to a theoretical model (Fig. S1(b)); ii) then, we use the fitting as a theoretical reference for subtracting the phonon contribution from all measurements. Our theoretical model includes both Debye (acoustic) and Einstein (optical) contributions, and reads:

$$c_p(T) = \sum_i w_{D,i} 9R \left(\frac{\theta_{D,i}}{T}\right)^3 \int_0^{\theta_{D,i}/T} \frac{y^4 \exp(y)}{(\exp(y) - 1)^2} dy + \sum_i w_{E,i} 3R \frac{(\theta_{E,i}/T)^2 \exp(\theta_{E,i}/T)}{(\exp(\theta_{E,i}/T) - 1)^2}$$

where $R$ is the universal gas constant, $\theta_{D,i}$ and $\theta_{E,i}$ are, respectively, the Debye and Einstein temperatures for a given mode $i$ and $w_{D,i}$ and $w_{E,i}$ are the relative weights of the contribution of the acoustic, or optical, phonon mode $i$ to the heat capacity. Our system is comprised of 10 atoms per formula unit, giving rise to 30 vibrational modes, 3 of which are acoustic modes and the remaining 27 are optical modes. We will adopt the approximation that all these modes are taken into account by 1 acoustic mode and 3 distinct optical modes. The best fitting was obtained in the
Figure 2. Fittings of the low $T$ region ($0.2 \leq T \leq 1.0$ K) of $C_{\text{mag}}(T)$ data to the expression: $C_{\text{mag}}(T) = \gamma(H)T^{\alpha(H)}$ for different values of $H$

Now, we turn our attention to $C_{\text{mag}}$. The behavior of $C_{\text{mag}}$ at low $-T$ is key to characterize our proposed SL phase. In the main text (Fig. 2), we reported $\alpha(H)$ and $\gamma(H)$ parameters obtained by fitting $C_{\text{mag}}$ to the expression:

$$C_{\text{mag}}(T) = \gamma(H)T^{\alpha(H)}$$

the fitting considered the following data range $0.2 \leq T \leq 1.0$ K. In Fig. S2 we show the fitting results in detail.

As discussed in the main text, the presence of uncorrelated magnetic trimers would imply the appearance of sizeable Schottky anomalies in the field dependent measurements of the magnetic heat capacity $C_{\text{mag}}$. Here we show the details of this discussion. We will also present the results for the dimer contribution, showing that it can be ignored in the low-$T$ region.

Adopting the experimentally determined $J_1$ and $J_2$ values and Hamiltonians in Eqs. (2) and (1) (including an extra Zeeman term), the energy levels of the magnetic trimer and dimer states can be calculated. The results are then applied to calculate the contribution of the magnetic trimers to $C_{\text{mag}}$:

$$C_{\text{mag}} = \frac{\partial}{\partial T} \sum_n E_n \exp(-E_n/k_BT)$$

Results are presented in Fig. S3(a)-(b). As expected, dimers do not present the anomaly for its ground state is a singlet. Furthermore, the dimer contribution to the total entropy in this temperature range is negligible since
Figure 3. Theoretical analysis of the magnetic heat capacity due to dimers and trimers and comparison to experimental data. (a)-(b) Dimer and trimer contribution to the magnetic heat capacity as a function of $H$ (energy levels calculated from the Hamiltonians given by Eqs. 2 1, experimentally determined $J_1$ and $J_2$). Both contributions are negligible for $H = 0$. Furthermore, up to $T = 15$ K the dimer contribution can always be neglected. (c) Comparison between the calculated trimer Shottky anomaly and experimental data.

$C_{\text{dimer}} \approx 0$ (and the entropy recovering associated do the dimer formation takes place at higher temperature). The trimer, however, would present a sizeable contribution that can be compared with experimental data. This comparison is presented in Fig. S3(c) for $H = 1$T and $H = 9$ T. At this selected fields, it is clear that the sole contribution of the trimer would be larger than $C_{\text{mag}}$. In conclusion, it is suggested once again that the magnetic trimers are part of the proposed correlated state.
III. µSR

A. Dynamic spin susceptibility

Now we present details of a brief quantitative analysis of the µSR experimental results. Our aim is to estimate the spin fluctuation rate for temperatures above and below the crossover. Here, we closely follow the discussion of Refs. [3, 4]. The spin fluctuation rate $\nu$ for $T > 10$ K can be estimated as:

$$\nu_{T>10\text{ K}} = \frac{zJS}{h}$$

where $z$ is the coordination number of the magnetic lattice, $J$ is the exchange constant, $S$ is the spin of the magnetic specimen and $h$ the Planck constant. In reference to Fig.1(c) of the main text, $z = 6$. In a mean field approximation, $J$ can be calculated from $\theta_{orp} = -7.3$ K as:

$$\theta_{orp} = \frac{zJS(S+1)}{3}$$

The results are $J \approx 0.97$ K and $\nu_{T>10\text{ K}} = 7.4(1) \times 10^{10}$ Hz as written in the main text. Another parameter of interest is the field distribution width $\Delta$. In general:

$$\lambda(H) = \frac{2\nu\Delta^2}{\nu^2 + (\mu_0 H^2 \gamma_\mu)^2}$$

where $\lambda$ is the nearly $T$–independent relaxation rate for $T > 10$ K ($\lambda \approx 0.07$ $\mu$s$^{-1}$, see Fig. 4(c) of the main text), $\mu_0 H$ is the applied magnetic field (which is 0) and $\gamma_\mu$ is the muon giromagnetic factor (135.5 MHz/T). We obtain $\Delta = 5.09 \times 10^7$ Hz.

The above equations are not appropriate for the low–$T$ region. Indeed, it is expected that at low–$T$, the spin dynamic autocorrelation function $S(t)$ will be $S(t) \propto (\tau/t)^x \exp(-\nu t)$ with $x \neq 0$, since the system is not a simple paramagnet. In this case, the formula for $\lambda(H)$ assumes the following form [4]:

$$\lambda(H) = 2\Delta^2 \tau^x \int_0^\infty t^{-x} \exp(-\nu_{T<1.5\text{ K}} t) \cos(2\pi \mu_0 \gamma_\mu H t) dt$$

where $\tau$ is early time cutoff, $\Delta$ is the new field distribution width (for the low–$T$ region), $x$ is a critical exponent and $1/\nu$ is the late time cutoff (spin fluctuation rate). The experimental values for $\lambda(H)$ are extracted from the LF experiments. The obtained parameters are $x = 0.64(3)$ and $\nu_{T<1.5\text{ K}} = 3.7(6) \times 10^6$ Hz. This is a decrease of about 4 orders of magnitude when compared with $\nu_{T>10\text{ K}}$. Fig S4 show the data and the fitting. This result should be taken with care in view of the small amount of data points for distinct field values in the LF experiments. Nevertheless, it suggests long-time spin correlations at low–$T$ in our system which, in turn, can be interpreted as the formation of an entangled spin state in the system.

[1] F. A. Garcia, U. F. Kaneko, E. Granado, J. Sichelschmidt, M. Hölzel, J. G. S. Duque, C. A. J. Nunes, R. P. Amaral, P. Marques-Ferreira, and R. Lora-Serrano, Physical Review B 91, 224416 (2015).
[2] M. T. Causa, M. Tovar, A. Caneiro, F. Prado, G. Ibanez, C. A. Ramos, A. Butera, B. Alascio, X. Obradors, S. Pinol, et al., Physical Review B 58, 3233 (1998).
[3] Y. J. Uemura, A. Keren, K. Kojima, L. P. Le, G. M. Luke, W. D. Wu, Y. Ajiro, T. Asano, Y. Kuriyama, M. Mekata, H. Kikuchi, and K. Kakurai, Physical Review Letters 73, 3306 (1994).
[4] Y. Li, D. Adroja, P. K. Biswas, P. J. Baker, Q. Zhang, J. Liu, A. A. Tsirlin, P. Gegenwart, and Q. Zhang, Physical Review Letters 117, 097201 (2016).
Figure 4. Relaxation rate as a function of $H$ (crossed circles) and the fitting of $\lambda(H)$ as discussed in the text.

Parameters

$x = 0.64(3)$

$\nu_{T<1.5K} = 3.7 \times 10^6$ Hz

$2\Delta^2\tau^x = 0.8(1)$ Hz