

Bose-Einstein condensation of triplons in the $S = 1$ tetramer antiferromagnet $\text{K}_2\text{Ni}_2(\text{MoO}_4)_3$: A compound close to quantum critical point

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Abstract

The structure of $\text{K}_2\text{Ni}_2(\text{MoO}_4)_3$ consists of $S = 1$ tetramers formed by Ni^{2+} ions. The magnetic susceptibility $\chi(T)$ and specific heat $C_P(T)$ data on a single crystal show a broad maximum due to the low-dimensionality of the system with short-range spin correlations. A sharp peak is seen in $\chi(T)$ and $C_P(T)$ at about 1.13 K, well below the broad maximum. This is an indication of magnetic long-range order *i.e.*, the absence of spin-gap in the ground state. Interestingly, the application of a small magnetic field ($H > 0.1$ T) induces magnetic behavior akin to Bose-Einstein condensation (BEC) of triplon excitations observed in some spin-gap materials. Our results demonstrate that the temperature-field ($T - H$) phase boundary follows a power-law ($T - T_N$) $\propto H^{1/\alpha}$ with the exponent $1/\alpha$ close to $2/3$, as predicted for BEC scenario. The observation of BEC of triplon excitations in small H infers that $\text{K}_2\text{Ni}_2(\text{MoO}_4)_3$ is located in the proximity of a quantum critical point, which separates the magnetically ordered and spin-gap regions of the phase diagram.

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Spin-gap materials exhibit remarkably exotic magnetic phenomena such as the realizations of Bose-Einstein condensation (BEC) and appearance of magnetization plateaus [1–5]. In general, spin-gap materials have a singlet ($S = 0$) ground state and the triplet excited states are separated from the ground state by an energy gap, called the spin-gap. With increasing magnetic field (which leads to a Zeeman splitting of $S = 1$ states), at a critical value of the field H_c , the lowest sub-state of the triplet ($S_z = 1$) crosses the $S = 0$ ground state. As a result, a finite concentration of triplets (triplons) populate. This consequently leads to several field-induced magnetic long-range-ordering (LRO) phenomena such as BEC of triplons in the vicinity of $T = 0$ K and H_c [1, 2]. In this context, the applied magnetic field (H) acts as a chemical potential in separating the spin-gap region and LRO region of the quantum phase diagram at $T \rightarrow 0$ K [6]. Experimentally, the field-induced BEC of triplon behavior has been intensively studied for various spin-gap materials with $S = 1/2$ dimers TlCuCl_3 [7, 8], $\text{BaCuSi}_2\text{O}_6$ [9, 10], $\text{Sr}_3\text{Cr}_2\text{O}_8$ [11, 12], $\text{Ba}_3\text{Cr}_2\text{O}_8$ [13]. Recently, BEC of triplet and quintuplet excitations have also been observed above the critical fields 8.7 T, and 32.42 T, respectively, in the $S = 1$ dimer compound $\text{Ba}_3\text{Mn}_2\text{O}_8$ [14, 15]. On the other hand, BEC of magnons has been

observed in other class of materials with magnetic-LRO including, yttrium–iron–garnet films at room temperature via microwave pumping [16], Cs_2CuCl_4 [17] and Gd nanocrystalline samples [18, 19]. In the case of Cs_2CuCl_4 , although the material undergoes a magnetic transition (T_N) at 0.595 K, the gap in the magnon spectrum closes at about 8.51 T and the three dimensional (3D) BEC phase boundary relation $T_N \propto (H - H_c)^{1/\alpha}$ with an exponent $1/\alpha = 2/3$ is observed, similar to other spin-gap materials [7–15]. Interestingly, when a spin-gap system is subjected to significant three-dimensional interactions, the triplet states are broadened and thus reduce the size of the spin-gap. In such a case, a small H_c is enough to induce BEC of triplon excitations. This class of material offers an ideal ground to explore quantum critical phenomena in the proximity of a Quantum Critical Point (QCP) in view of their collective spin excitations, high homogeneity in boson density, and topological order [1].

In this Rapid Communication, we study a new kind of antiferromagnetic material $\text{K}_2\text{Ni}_2(\text{MoO}_4)_3$, which exhibits magnetic LRO, through the comprehensive thermodynamic studies on single crystals. Interestingly, it exhibits a field-induced BEC of triplon excitations at low magnetic fields. Being a non-spin-gap material, this quantum magnet pose to host exotic magnetic excitations and is located close to a QCP.

The polycrystalline samples of the titled material were prepared using K_2CO_3 , NiO , and MoO_3 . A mixture of these chemicals with the stoichiometric molar ratio of

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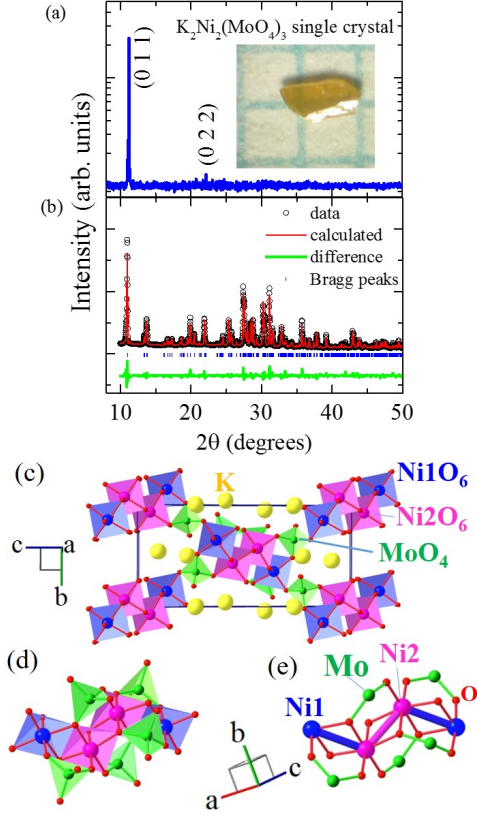


Figure 1: (Color online) (a) XRD pattern of a single crystal of $\text{K}_2\text{Ni}_2(\text{MoO}_4)_3$ with the x-ray beam perpendicular to the $(0ll)$ planes. Inset shows an image of the single crystal. The top surface is a $(0ll)$ plane. (b) Rietveld refinement of the XRD data of polycrystalline samples. (c) The crystal structure of $\text{K}_2\text{Ni}_2(\text{MoO}_4)_3$ viewed along a -direction. (d) The $S = 1$ tetramers are constructed by Ni_1O_6 (blue) and Ni_2O_6 (pink) octahedra. The MoO_4 tetrahedral units (green) also mediated the Ni-Ni couplings in a tetramer. (e) Tetramers in the atoms and bonds representation.

1:2:3 was fired for 24 hrs with a heating rate of 60°C per hour to reach 600°C . The single crystals were grown using K_2MoO_4 flux agent (see inset of Fig. 1(a)). The x-ray diffraction (XRD) measurements were done on both the single crystal and polycrystalline sample. The identified peaks, which correspond to $(0ll)$ planes of the $\text{K}_2\text{Ni}_2(\text{MoO}_4)_3$ phase [20] are shown in Fig. 1(a). In order to extract the unit cell lattice parameters, we have employed the Rietveld refinement analysis on the polycrystalline sample with the Fullprof Suite program [21] using the initial structural parameters provided by R. F. Klevtsova, *et al.* in Ref. [20] (see Fig. 1(b)). The obtained residual refinement factors R_P , R_{wp} , R_{exp} , and χ^2 are 0.177, 0.180, 0.035, and 5.1, respectively. The lattice parameters are found to be $a = 6.952(5)$ Å, $b = 8.910(7)$ Å, $c = 19.740(10)$ Å and $\beta = 108.065(5)^\circ$, consistent with the earlier reports [20].

The compound $\text{K}_2\text{Ni}_2(\text{MoO}_4)_3$ crystallizes in the prim-

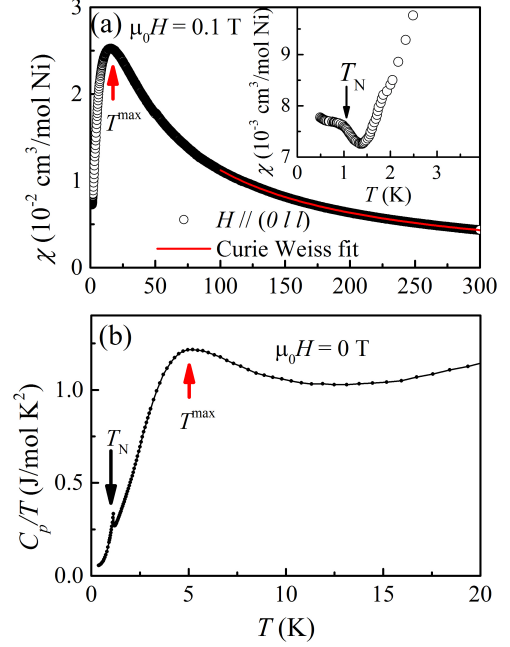


Figure 2: (Color online) (a) $\chi(T)$ of a single crystal with $H//(0ll)$. The red line is a fit to the Curie-Weiss law in the T -range 100–300 K. The inset shows the low- T data down to 500 mK. (b) The data of C_P/T in zero-field. The down-arrow indicates T_N , while the up-arrow points to the broad maximum (T^{max}).

itive monoclinic space group $P2_1/c$ (No. 14) containing $Z = 4$ formula units per unit cell (see Fig. 1(c)). The structure has $S = 1$ (Ni^{2+}) tetramers formed by two edge-shared Ni_1O_6 and Ni_2O_6 octahedra (see Fig. 1(c) and (d)). The bond angles of Ni-O-Ni are in between 94° to 98° , which naively suggests that the magnetic couplings might be antiferromagnetic in nature. In a tetramer unit, the Ni^{2+} ions are connected *via* MoO_4 tetrahedra, which might lead to the magnetic frustration through the next nearest neighbor (nnn) interactions in the tetramer. These $S = 1$ tetramers are also connected to each other through MoO_4 tetrahedral units running in all the three crystallographic directions, suggesting the presence of non-negligible three-dimensional (3D) interactions.

Magnetization (M) as a function of temperature (T) is measured on the single crystal in H parallel to $(0ll)$ plane. The magnetic susceptibility $\chi = (M/H)$ in the T -range 500 mK to 300 K is shown in Fig. 2(a). At high- T , the data follow the Curie-Weiss law with an effective magnetic moment (μ_{eff}) $\approx 3.34\mu_B$ and a Curie-Weiss temperature $\theta_{CW} \approx -25$ K. The obtained μ_{eff} value is larger than the expected value for $S = 1$ ($2.83\mu_B$), but is consistent with many Ni-based magnets [22, 23]. The obtained θ_{CW} of -25 K, indicates the presence of antiferromagnetic couplings between the Ni^{2+} ions. At low- T ,

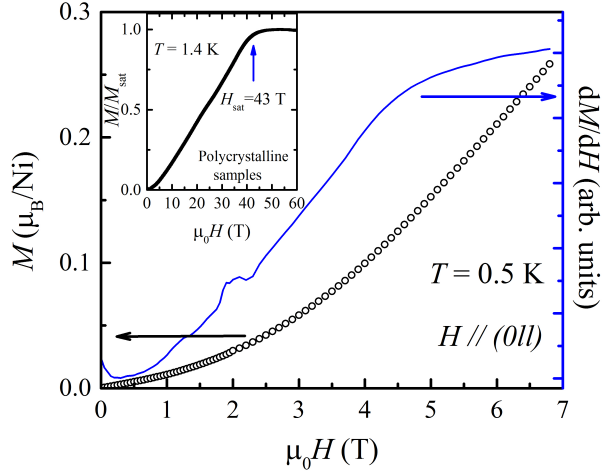


Figure 3: (Color online) (a) $M(H)$ up to 7 T at 0.5 K (left y -axis). dM/dH versus H is plotted on the right y -axis. Inset shows $M(H)$ data up to 60 T on a polycrystalline sample.

$\chi(T)$ shows a broad maximum around 16 K, indicative of short-range spin correlations possibly originating from the low-dimensionality of the system. Below the broad maximum, the susceptibility falls steeply down to 1.4 K and then has an upturn. Unlike the spin-gap behavior expected for isolated tetramer systems [20], the data deviate from the upturn at about 1.13 K, suggesting an antiferromagnetic transition (see inset of Fig. 2(a)). We have also measured the magnetization in H perpendicular to $(01l)$ plane, but no significant anisotropy was seen. Specific heat $C_P(T)$ data measured on a single crystal in zero-field are shown in Fig. 2(b). The data of C_P/T versus T show features similar to those observed in $\chi(T)$: a broad maximum at $T^{max} \approx 5$ K and a sharp transition at $T_N \approx 1.13$ K. The observed T^{max} of $C_P(T)$ is smaller than that of $\chi(T)$, as observed in other low-dimensional spin systems [25, 26]. The appearance of a sharp peak at T_N infers the presence of LRO possibly due to non-negligible inter-tetramer interactions.

To explore further the nature of magnetic phenomena of this quantum magnet, magnetization isotherm $M(H)$ was measured up to 7 T at $T = 0.5$ K ($< T_N$) as shown in Fig. 3. $M(H)$ data do not exhibit any hysteresis, ruling out the presence of ferromagnetic moment. In addition, the data show a non-linear behavior, unlike in a typical antiferromagnetic system. Similar non-linear behavior is also seen in low-fields ($H < 5$ T) in the $M(H)$ measured upto 60 T on the polycrystalline sample at 1.4 K, i.e., in the paramagnetic region ($T > T_N$), as shown in the inset of Fig. 3. The $M(H)$ data suggest the appearance of field-induced phenomenon in this quantum magnet. The magnetization increases with H and finally a fully polarized state with a saturated magnetization (M_{sat}) about $2 \mu_B / \text{Ni}$ ($M/M_{sat} = 1$) is observed beyond $H_{sat} = 43$ T.

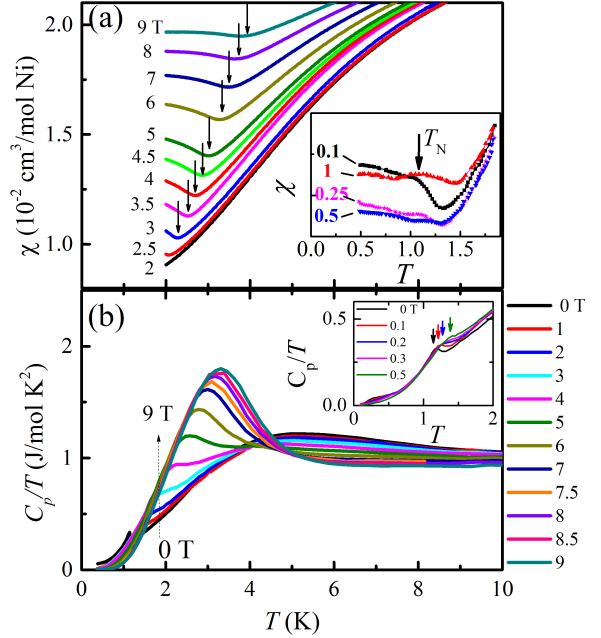


Figure 4: (Color online) (a) $\chi(T)$ data at 2 T to 9 T. The minima in $\chi(T)$ depicts a phase transition which could be reconciled as BEC of magnetic excitations. (b) C_P/T versus T for the fields from 0 T to 9 T. Inset shows the data at low-fields. The field-induced anomalies are represented by down arrows.

In order to understand the nature of field-induced phenomena in this material, we measured $\chi(T)$ on a single crystal in the T -range 2-300 K and $C_P(T)$ down to 70 mK under fields up to 9 T. As shown in the inset of Fig. 4(a), a small H of 0.25 T suppresses the $\chi(T)$ anomaly at T_N . On further increasing H , surprisingly, the $\chi(T)$ data move to higher- T and exhibit dip-like anomalies, which has been observed, so far, in several spin-gap materials exhibiting the field-induced BEC of triplons (when $H > H_C$) [1, 2]. The dip-like anomalies or minimum in $\chi(T)$ were also evidenced by theoretical simulations to support the BEC state of triplons [7]. Similarly, a cusp-like broad anomaly is observed in C_P/T data under a small H of 0.1 T (see inset of Fig. 4(b)). The anomaly also moves to higher temperature with increasing H . The observed transition and field-induced anomalies (T_{FI}) from $\chi(T)$ and $C_P(T)$ data at different fields are plotted in Fig. 5 (a), which separates the field-induced antiferromagnetic (FI-AFM) and paramagnetic (PM) regions. In order to evaluate the value of the critical exponent, the phase boundary is fitted with the equation $T_{FI} = T_N + aH^{1/\alpha}$, where a is a proportionality factor and α is an exponent. As suggested in the Ref. [27] that it is to be fitted below $T < 0.4 T_{FI}^{max}$ to get the precise exponent value. Here, T_{FI}^{max} is the maximum temperature at which a field-induced transition can take place (the plateau in

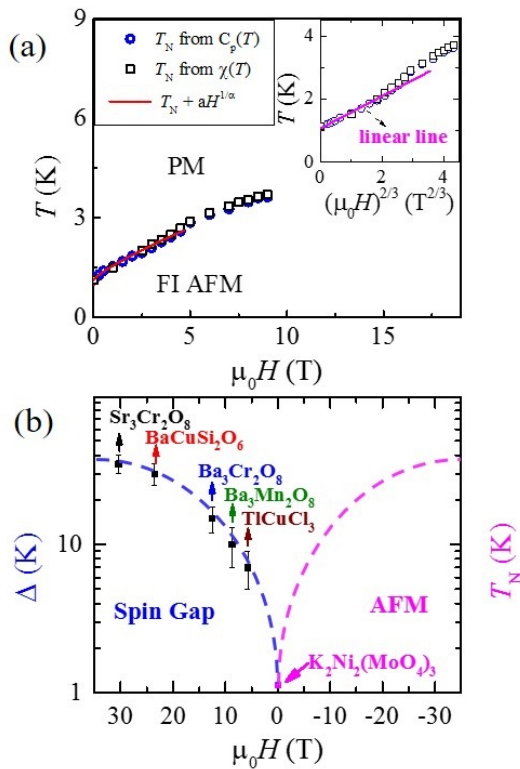


Figure 5: (Color online) (a) $T - H$ phase diagram of $\text{K}_2\text{Ni}_2(\text{MoO}_4)_3$. The red solid line is the fit mentioned in the text. Inset: the plot of T_N versus $H^{2/3}$. The pink line is an indication of linear behavior. (b) Schematic quantum phase diagram with H as tuning parameter. A QCP separates the spin-gap and the AFM-region. Some selected spin-gap compounds are on the left side of the phase diagram, while $\text{K}_2\text{Ni}_2(\text{MoO}_4)_3$ is positioned on the AFM-side.

the $T - H$ phase diagram). The obtained value of α is found to be 1.4 (1); rather close to the theoretical value of the exponent $3/2$ predicted for 3D BEC of universality class [27, 28]. Moreover, the T_{FI} values almost vary linearly with $H^{2/3}$ (see inset of 5(a)). The observed dip-like anomalies and the obtained α value suggest that the compound $\text{K}_2\text{Ni}_2(\text{MoO}_4)_3$ exhibits field-induced BEC behavior. It is interesting to notice that a very small field (0.1 T) is strong enough to induce this behavior in a system with zero-field LRO at 1.13 K.

To further understand the field-induced behavior, we have compared the data of a few spin-gap materials from literature which exhibit a BEC of triplons (see Table 1). So far, BEC behavior has been realized mostly in quantum mechanical spin-gap systems of the topological nature without any symmetry-breaking. Magnetic field acts as chemical potential and drives the density of triplons. As per the value of spin-gap and critical-fields, we have positioned them in the phase diagram in Fig. 5(b). The magnetic field acts as the tuning parameter and it drives the spin-gap ground state to the AFM state via the quantum critical point (QCP) at $T \rightarrow 0$ K. It can be seen that

Table I: Some details of spin-gap and antiferromagnetic materials.

Compound	Type	Δ or T_N (K)	H_c (T)	Ref.
$\text{Sr}_3\text{Cr}_2\text{O}_8$	$S = 1/2$ dimer	35	30.4	[12]
$\text{BaCuSi}_2\text{O}_6$	$S = 1/2$ dimer	30	23.5	[9, 10]
$\text{Ba}_3\text{Cr}_2\text{O}_8$	$S = 1/2$ dimer	15	12.5	[13]
$\text{Ba}_3\text{Mn}_2\text{O}_8$	$S = 1$ dimer	10	8.7	[15]
TiCuCl_3	$S = 1/2$ dimer	7	5.7	[7]
$\text{K}_2\text{Ni}_2(\text{MoO}_4)_3$	$S = 1$ tetramer	$T_N = 1.13$	≥ 0.1	this work

all the existing spin-gap materials are away from the QCP as a large value of H is required to suppress the spin-gap and finally to realize the field-induced phenomena. On the other hand, if any system is in the proximity of QCP then either the spin-gap and/or T_N approaches zero, as shown in Fig. 5. In such a case, a small critical H would be sufficient to perturb its state. As we have already observed that a small H induces behavior akin to BEC of triplon excitations, we conclude that $\text{K}_2\text{Ni}_2(\text{MoO}_4)_3$ is very close to the QCP on the AFM-side of the quantum phase diagram. We would also like to discuss the possibility that the ground state of $\text{K}_2\text{Ni}_2(\text{MoO}_4)_3$ might have a mixture of singlets and triplets (hence causes the LRO). Due to this reason, a small amount of Zeeman energy is required for the triplon excitations. In general, BEC corresponds to the spontaneous formation of a collective state with macroscopic number of bosons governed by a single wave function. In this antiferromagnet, the BEC of triplons state formed probably due to the coherent precession of transverse magnetization, which breaks $U(1)$ symmetry, at zero and finite fields. Whatever the origin of this unusual phenomena, the titled system experiences quantum mechanical fluctuations but orders at finite- T . It appears to be close to the quantum critical state *i.e.*, an extremely small gap or transition at low- T . The determination of coherence lengths via Inelastic Neutron Scattering measurements at zero-field and applied magnetic fields would be useful to further understand the BEC mechanism in this material.

We looked at several other magnetic models and the corresponding critical points. In the case of $S = 1/2$ dimers, the magnitude of the spin-gap (Δ) is same as that of the exchange coupling (J) [29]. But, the presence of significant inter-dimer coupling $J'/J = 0.7$ (which is at the QCP), as in the Shastry-Sutherland model, can stabilise an AFM state [30]. In the case of the $S = 1/2$ spin-ladder, the QCP is predicted to be at a relative strength $J'/J = 0.3$ [31]. Hence, we believe that a relative inter-tetramer strength in $\text{K}_2\text{Ni}_2(\text{MoO}_4)_3$ might have placed it at QCP. Moreover, the presence of nnn intra-tetramer couplings, which causes the magnetic frustration, does not seem to be negligible as the NiO_6 units are coupled to each other *via* MoO_4 units with the path Ni-O-Mo-O-Ni. The bond-angles of Ni-O-Mo, O-Mo-O, and Mo-O-Ni are about 116° , 113° , and 140° , respectively, which usually

favor AFM couplings (see Fig. 1 (d) & (e)). Magnetic frustration which usually enhance quantum fluctuations, perhaps also plays a crucial role in placing this antiferromagnet near a QCP. Further theoretical models would help to estimate the relative strength exchange couplings to understand the origin of quantum critical behavior.

In summary, we have successfully grown single crystals of the $S = 1$ tetramer system $\text{K}_2\text{Ni}_2(\text{MoO}_4)_3$ and investigated magnetization and specific heat studies. $\chi(T)$ and zero-field $C_P(T)$ reveal that $\text{K}_2\text{Ni}_2(\text{MoO}_4)_3$ exhibits LRO at 1.13 K due to the possible involvement of non-negligible 3D couplings, in contrast to the spin-gap behavior expected for an isolated tetramer system. However, a small H of about 0.1 T induces a change in the magnetic behavior. The field-induced transition temperature increases with increasing H and follows $H^{1/\alpha}$ behavior with $\alpha = 1.4(1)$, which suggests that the observed field-induced phenomena might be related to the BEC of triplons as observed in other spin-gap materials. Despite

having LRO in zero-field, the field-induced behavior even in low-fields might point towards condensation of triplon excitations with the possibility that $\text{K}_2\text{Ni}_2(\text{MoO}_4)_3$ is located in the vicinity of a quantum critical point in the phase diagram. The ground state might have a mixture of singlets and triplets, due to which, a small H could induce BEC excitations in this material. We believe that our results will draw attention to explore more insights into the quantum criticality of the titled material.

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- [1] T. Giamarchi, Ch. Rüegg, and O. Tchernyshyov, *Nat. Phys.* **4**, 198 (2008).
- [2] V. Zapf, M. Jaime, and C.D. Batista, *Rev. Mod. Phys.* **86**, 563 (2014); Erratum *Rev. Mod. Phys.* **86**, 1453 (2014).
- [3] H. Kageyama, K. Yoshimura, R. Stern, N. V. Mushnikov, K. Onizuka, M. Kato, K. Kosuge, C. P. Slichter, T. Goto, and Y. Ueda, *Phys. Rev. Lett.* **82**, 3168 (1999).
- [4] K. Onizuka, H. Kageyama, Y. Narumi, K. Kindo, Y. Ueda, and T. Goto *J. Phys. Soc. Jpn.* **69**, 1016 (2000).
- [5] K. Kodama, M. Takigawa, M. Horvatić, C. Berthier, H. Kageyama, Y. Ueda, S. Miyahara, F. Becca, F. Mila, *Science* **298**, 395 (2002).
- [6] S. Sachdev, *Quantum Phase Transitions* (Cambridge University Press, Cambridge, 1999).
- [7] T. Nikuni, M. Oshikawa, A. Oosawa, and H. Tanaka, *Phys. Rev. Lett.* **84**, 5868 (2000).
- [8] P. Merchant, B. Normand, K. W. Krämer, M. Boehm, D. F. McMorrow, and Ch. Rüegg, *Nature Physics* **10**, 373 (2014).
- [9] S. E. Sebastian, P. A. Sharma, M. Jaime, N. Harrison, V. Correa, L. Balicas, N. Kawashima, C. D. Batista, and I. R. Fisher, *Phys. Rev. B* **72**, 100404 (2005).
- [10] M. Jaime, V. F. Correa, N. Harrison, C. D. Batista, N. Kawashima, Y. Kazuma, G. A. Jorge, R. Stein, I. Heinmaa, S. A. Zvyagin, Y. Sasago, and K. Uchinokura, *Phys. Rev. Lett.* **93**, 087203 (2004).
- [11] Y. Singh and D. C. Johnston, *Phys. Rev. B* **76**, 012407 (2007).
- [12] A. A. Aczel, Y. Kohama, C. Marcenat, F. Weickert, M. Jaime, O. E. Ayala-Valenzuela, R. D. McDonald, S. D. Selesnic, H. A. Dabkowska, and G. M. Luke, *Phys. Rev. Lett.* **103**, 207203 (2009).
- [13] A. A. Aczel, Y. Kohama, M. Jaime, K. Ninios, H. B. Chan, L. Balicas, H. A. Dabkowska, and G. M. Luke, *Phys. Rev. B* **79**, 100409 (2009).
- [14] M. Uchida, H. Tanaka, M.I. Bartashevich, and T. Goto, *J. Phys. Soc. Jpn.* **70**, 1790 (2001).
- [15] E. C. Samulon, Y. Kohama, R. D. McDonald, M. C. Shapiro, K. A. Al-Hassanieh, C. D. Batista, M. Jaime, and I. R. Fisher, *Phys. Rev. Lett.* **103**, 047202 (2009).
- [16] S. O. Demokritov, V. E. Demidov, O. Dzyapko, G. A. Melkov, A. A. Serga, B. Hillebrands, and A. N. Slavin, *Nature (London)* **443**, 430 (2006).
- [17] T. Radu, H. Wilhelm, V. Yushankhai, D. Kovrizhin, R. Coldea, Z. Tylczynski, T. Luhmann, and F. Steglich, *Phys. Rev. Lett.* **95**, 127202 (2005).
- [18] S. N. Kaul, and S. P. Mathew, *Phys. Rev. Lett.* **106**, 247204 (2011).
- [19] S. N. Kaul, *Phys. Status Solidi B* **248**, 2276 (2011).
- [20] R. F. Klevtsova and L. A. Inskaya, *Zhurnal Strukturnoi Khimii*, **23**, 176 (1982).
- [21] Juan Rodriguez-Carvajal, *Physica B* **192**, 55 (1993).
- [22] J. Hwang, E. S. Choi, F. Ye, C. R. Dela Cruz, Y. Xin, H. D. Zhou, and P. Schlottmann, *Phys. Rev. Lett.* **109**, 257205 (2012).
- [23] Arvind Yogi, A. K. Bera, Arvind Maurya, Ruta Kulkarni, S. M. Yusuf, A. Hoser, A. A. Tsirlin, and A. Thamizhavel *Phys. Rev. B* **95**, 024401 (2017).
- [24] R. Becker, M. Johnsson, R. K. Kremer, H.-H. Klauss, and P. Lemmens, *J. Am. Chem. Soc.*, **128**, 15469 (2006).
- [25] B. Koteswararao, S. Salunke, A. V. Mahajan, I. Dasgupta, and J. Bobroff, *Phys. Rev. B* **76**, 052402 (2007).
- [26] B. Koteswararao, S. K. Panda, R. Kumar, Kyongjun Yoo, A. V. Mahajan, I. Dasgupta, B. H. Chen, Kee Hoon Kim, and F. C. Chou, *J. Phys: Condens. Matter* **27**, 426001 (2015).
- [27] O. Nohadani, S. Wessel, B. Normand, and S. Haas, *Phys. Rev. B* **69**, 220402 (2004).
- [28] T. Giamarchi and A. M. Tsevlík, *Phys. Rev. B* **59**, 11398 (1999).
- [29] D.C. Johnston, R.K. Kremer, M. Troyer, X. Wang, A. Klümper, S.L. Bud'ko, A.F. Panchula, and P.C. Canfield, *Phys. Rev. B* **61**, 9558 (2000).
- [30] S. Miyahara, and K. Ueda, *Phys. Rev. Lett.*, **82**, 3701 (1999).
- [31] S. Sachdev, *Science* **288**, 475 (2000).