Glassy Spin Freezing and Gapless Spin Dynamics in a Spatially Anisotropic Triangular Antiferromagnet \( \text{Ag}_2\text{MnO}_2 \)

S. Ji,1,2 J.-H. Kim,1 Y. Qiu,2 M. Matsuda,3 H. Yoshida,4 Z. Hiroi,4 M. A. Green,5 and S.-H. Lee1,

1Department of Physics, University of Virginia, Charlottesville, VA 22904-4714, USA
2NIST Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, MD 20899, USA
3Quantum Beam Science Directorate, Japan Atomic Energy Agency (JAEA), Tokai, Ibaraki 319-1195, Japan
4Institute for Solid State Physics, University of Tokyo, Kashiwa, Chiba 277-8581, Japan
5Institut Laue Langevin, Boste Postale 156, F-38042 Grenoble Cedex 9, France

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Using elastic and inelastic neutron scattering techniques, we show that upon cooling a spatially anisotropic triangular antiferromagnet \( \text{Ag}_2\text{MnO}_2 \) freezes below \( T_g \approx 50 \text{ K} \) into short range collinear state. The static spin correlations are extremely two-dimensional, and the spin fluctuations are gapless with two characteristic relaxation rates that behave linearly with temperature.

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Since a quantum mechanical valence bond state was proposed as the ground state of triangular antiferromagnets in 1970s [1], triangular lattice systems have been extensively studied, theoretically and experimentally. For the spatially isotropic triangular system, there is now a consensus that even quantum spins are magnetically ordered with the 120° spiral structure of the classical state. Recently interests in the field focus on further neighbor interactions, multi-spin interactions, and spatial anisotropy that may lead to more exotic states [2, 3, 4, 5, 6, 7, 8]. The spatially anisotropic triangular antiferromagnet with stronger exchange coupling \( J \) along a chain direction and weaker frustrated zig-zag \( J' \) between the chains is interesting because we can also study the effects of the one- to two-dimensional cross-over, but the nature of the ground state is unclear [2, 3, 4, 5, 6, 7, 8].

Experimental studies on the spatially anisotropic triangular system have been limited because of scarcity of model systems. The most studied compound is \( \text{Cs}_2\text{CuCl}_4 \) (\( s = 1/2 \)) that exhibits a gapless excitation spectrum at low temperatures which was attributed to \( s = 1/2 \) spinon excitations [3]. For \( T < 0.17 |\Theta_{\text{CW}}| \) (\( \Theta_{\text{CW}} \) the Curie-Weiss temperature), finite interlayer couplings, \( J' = 0.045 J \), drive the system into long range incommensurate spiral order [10]. For a larger spin, \( \text{NaMnO}_2 \) (\( s = 2 \)) has recently been shown to have long range collinear order with a gapped excitation spectrum below \( T_N \approx 0.092 |\Theta_{\text{CW}}| \) [11, 12]. In these systems, the neighboring magnetic triangular planes are separated by a single non-magnetic layer and weak interplane interactions cause the observed long range orders at low temperatures.

More recently, \( \text{Ag}_2\text{MnO}_2 \) was synthesized as a promising candidate for the triangular antiferromagnet where magnetic \( \text{MnO}_2 \) layers are separated by nonmagnetic \( \text{Ag} \) bilayers [13]. Bulk susceptibility data showed that the \( \text{Mn}^{3+} \) ions possess an effective moment of \( p_{\text{eff}} = 4.93 \mu_B \), which is consistent with the high spin \( s = 2 \) state of the \( \text{Mn}^{3+}(t^2_g)^{2}e^1_g \) ion. Although \( \Theta_{\text{CW}} \approx 400 \text{ K} \), indicating strong antiferromagnetic interactions, no long range order was observed down to \( 2 \text{ K} \), suggesting strong frustration. Below \( T_g = 22 \text{ K} \approx 0.05 |\Theta_{\text{CW}}| \), on the other hand, a field-cooled and zero-field-cooled hysteresis was observed in the bulk susceptibility measurements, which is indicative of a spin freezing [13].

In this letter, we report our elastic and inelastic neutron scattering measurements on a powder sample of \( \text{Ag}_2\text{MnO}_2 \). Our principal results are the following. (1) Upon cooling, it undergoes a structural phase transition at \( T = 540 \text{ K} \) from trigonal to monoclinic due to a ferro-orbital order of the Jahn-Teller active \( \text{Mn}^{3+} \) ion. This results in spatially anisotropic magnetic interactions in the triangular plane. (2) Despite the large \( \Theta_{\text{CW}} \), it does not order down to \( T_f = 48(6) \text{ K} \) below which the Mn spins freeze into a collinear spin state with the frozen moment, \( \langle M \rangle = 2.4(2) \mu_B/\text{Mn} << gs\mu_B/\text{Mn} \). (3) The frozen spin order is short ranged with anisotropic in-plane correlation lengths of \( \xi_b = 18.9(37) \text{ Å} \) and \( \xi_e = 5.9(18) \text{ Å} \) and an out-of-plane correlation length of \( \xi_c = 1.6(16) \text{ Å} \), indicating extreme two-dimensionality. (4) The two-dimensional spin fluctuations have a gapless spectrum with two characteristic relaxation rates, an overall relaxation rate, \( \Gamma_0 \), and a lower limit, \( \Gamma_1 \), that behave linearly above \( T_g \) and \( T_f \), respectively. We argue that \( \text{Ag}_2\text{MnO}_2 \) might be an excellent candidate for a gapless spin liquid phase.

A 2 g powder sample of \( \text{Ag}_2\text{MnO}_2 \) was prepared at the ISSP of the University of Tokyo using the solid-state reaction technique with stoichiometric mixture of \( \text{Ag} \) and \( \text{MnO}_2 \) powder. A series of neutron scattering measurements were performed at the NIST Center for Neutron Research (NCNR). Time-of-flight neutron scattering measurements were carried out using the disk chopper spectrometer (DCS) with wavelengths of \( \lambda = 1.8 \text{ Å}, 2.9 \text{ Å} \) and \( 4.8 \text{ Å} \). Neutron powder diffraction (NPD) measurements were performed on the BT1 powder diffractometer with a Cu(311) monochromator (\( \lambda = 1.5403 \text{ Å} \)), and Rietveld refinement was carried out using FULLPROF program [14]. Temperature dependence of the nuclear Bragg peaks was studied at TAS-2 located at the JRR-3...
As shown in Fig. 1 (a), at 580 K the nuclear Bragg reflection positions tell us that the high temperature crystal structure is trigonal with \( R\bar{3}m \) symmetry. The \((0,0,L)\) reflections are instrument resolution limited, however, much broader than the \(Q\)-resolution. The best fit as shown as the line was obtained with the lattice parameters listed in Table I and the stacking correlation length of 217(37) Å. As shown in Fig. 1 (c), the chemical unit cell of the perfect hexagonal structure consists of three \( \text{MnO}_2 \) layers (A, A’ and A”) and three Ag bi-layers (B, B’ and B”) that appear alternately. Neighboring layers of same kind are displaced by \((1/3,1/3,1/3)\). The stacking faults may occur due to weak Ag-O van der Waals and ionic bondings between the Ag bi-layer and the neighboring \( \text{MnO}_2 \) layer (see Fig. 1 (c)). Thus, the stacking order of the layers can be imperfect; instead of the long range stacking of A-B-A’B’-A”B” as expected in a perfect crystal, stacking faults such as A-B-A’B’-A”B or A-B’-A-B-A’-B may occur. Such stacking faults will not change the \(c\)-positions of the layers but disorder the arrangements of the \(ab\)-positions of the atoms along the \(c\)-axis, and yield the observed broadenings of the \((H \neq 0, K \neq 0, L)\) nuclear Bragg reflections.

Upon cooling from 580 K, the two Bragg reflections over \( 2.4 \, \text{Å}^{-1} \leq Q < 2.6 \, \text{Å}^{-1} \) split into five peaks at \( \sim 540 \, \text{K} \), indicating lowering of the crystal symmetry (see the inset of Fig. 1 (b)). The best refinement of the NPD data taken at 300 K (Fig. 1 (b)) was obtained with a monoclinic \( C2/m \) crystal structure with the lattice parameters listed in Table I. The lattice distortion is due to Jahn-Teller distortion of the \( \text{MnO}_6 \) octahedron that involves elongation of a local axis that is close to the \(a\)-axis, as shown in Fig. 1 (d) and Fig. 3 (b). As a result, the \(e_g\) electrons of \( \text{Mn}^{3+} \) ions occupy \( d_{3\gamma-2z^2} \) orbital, resulting in a ferro-orbital order (see Fig. 3 (b)).

**TABLE I**: The crystal structural parameters of \( \text{Ag}_2\text{MnO}_2 \) obtained at 580 K and 300 K by refining the data shown in Fig. 1 using the program Fullprof.

| Atom(W) | \( x \) | \( y \) | \( z \) |
|---------|--------|--------|--------|
| \( 580 \, \text{K (}R\bar{3}m) \), \( \chi^2 = 3.92, R_{wp} = 12.1 \) | \( a = b = 2.96991(18)\,\text{Å}, \, c = 26.14007(229)\,\text{Å} \) | \( \text{Ag (6c)} \) | 0 | 0 | 0.21064(20) |
| \( \text{Mn (3a)} \) | 0 | 0 | 0 |
| \( \text{O (6c)} \) | 0 | 0 | 0.29552(26) |
| \( \text{Mn-O} = 1.9831(4)\,\text{Å} \) | 300 K (\( C2/m \)), \( \chi^2 = 5.48, R_{wp} = 15.0 \) | \( a = 5.24722(60)\,\text{Å}, \, b = 2.88226(16)\,\text{Å}, \, c = 8.89877(99)\,\text{Å} \) | \( \beta = 102.39862(1300)^{\circ} \) |
| \( \text{Ag (4i)} \) | 0.21183(206) | 0 | 0.62875(73) |
| \( \text{Mn (2a)} \) | 0 | 0 | 0 |
| \( \text{O (4i)} \) | 0.30348(229) | 0 | 0.88331(91) |
| \( \text{Mn-O (apical)} = 2.079(6)\,\text{Å}, \, \text{Mn-O (plane)} = 1.939(2)\,\text{Å} \) |
Here $S_{\perp}(Q)$, the unit cell magnetic structure factor normal to the scattering vector, can be written as

$S_{\perp}(Q) = F(Q)^2 \sum_{\nu} M_{\nu}^{\perp} e^{-iQ \cdot r_{\nu}}$ where $M_{\nu}$ and $r_{\nu}$ are the staggered magnetic moment and position of Mn$^{3+}$ ion at site $\nu$, respectively, and $F(Q)$ is the Mn$^{3+}$ magnetic form factor. $\xi_\alpha$ and $\hat{r}_\alpha$ are the spin correlation length and the unit lattice vector along the $\alpha$-axis, respectively. The best fit shown as the red solid line in Fig. 3 (a) was obtained with $\xi_b = 18.9(37)$ Å along the chain, $\xi_a = 5.9(18)$ Å perpendicular to the chain in the triangular plane, and a negligible out-of-plane correlation length of $\xi_c = 1.6(16)$ Å. For comparison, we also show the calculated $S(Q)$ obtained with the same $\xi_b$ and $\xi_b$ but $\xi_c$ to be the inter-layer distance between the neighboring triangular layers, 8.9 Å (see the blue dashed line), which does not reproduce the data. These clearly indicate that the magnetic interactions in Ag$_2$MnO$_2$ are extremely two-dimensional, as expected by the large distance between the MnO$_2$ layers that are separated by the non-magnetic Ag $b$-layers. The anisotropic inplane correlation lengths can be understood when the orbital state of Mn$^{3+}$ ($t_{2g}^{-1}e_g^1$) ions are considered.\cite{13,20} As shown in Fig. 3 (b), in the ferromagnetic state the $e_g$ electrons do not induce any obvious superexchange paths between Mn-Mn ions. On the other hand, due to the edge-sharing network of the MnO$_6$ octahedra neighboring $t_{2g}$ electrons directly overlap, inducing strong nearest neighbor (NN) interactions that is sensitive to the distance, $d$, between the Mn ions. The lattice
FIG. 4: (Color online) (a)-(c) Energy dependence of the imaginary part of the dynamic susceptibility obtained by integrating and converting the inelastic neutron scattering intensity \( I(Q, \omega) \) shown in Fig. 2 over 1 \( \Lambda^{-1} < Q < 2 \Lambda^{-1} \) at (a) 100 K, (b) 40 K, and (c) 1.5 K. (d) Relaxation rate, \( \Gamma \), as a function of temperature. Lines are described in the text.

distortion shown in Fig. 3 (b) leads to stronger intrachain exchange coupling \( J \) with \( d \approx 2.88 \) Å and four weaker zig-zag coupling \( J' \) with \( d \approx 2.99 \) Å as shown by dark and light blue lines, respectively.

Let us now turn to the nature of the dynamical spin correlations. We obtained energy dependence of the scattering intensity, \( I(\omega) \), by integrating all \( I(Q, \omega) \) data taken with \( \lambda = 1.8 \) Å, 2.8 Å and 4.9 Å over 1 \( \Lambda^{-1} < Q < 2 \Lambda^{-1} \). Then, using the detailed balance relation \( \chi''(\omega) = \frac{\Gamma_1}{\pi} (1 - \exp^{-\hbar \omega/k_B T}) I(\omega) \) where \( \hbar \) is the Boltzmann constant and the imaginary part of the dynamic susceptibility, \( \chi'' \), was extracted. As shown in Fig. 4 (a), at \( T_f < 100 \) K \( \ll |\Theta_{CW}|, \chi''(\omega) \) can be well fitted to a lorentzian, \( \chi''(\omega) \propto \Gamma_\omega/\Gamma_0^2 + \omega^2 \). When temperature decreases, however, the spectral weight shifts down to lower energies and the lorentzian cannot reproduce the low energy region while it fits the higher energy region. Below \( T_f \), the low energy region can be fit to \( \chi''(\omega) \propto \tan^{-1}(\omega/\Gamma_1) \) that represents spin relaxations with a distribution of the relaxation rates with the lower limit being \( \Gamma_1 \). The optimal relaxation rates are plotted in Fig. 4 (d). For \( T > T_g \), the overall relaxation rate \( \Gamma_0 = C_0 (k_BT)^{-\alpha_0} \) with \( C_0 = 0.5(1) \) and \( \alpha_0 = 1.08(16) \). For \( T > T_f \), the lower limit \( \Gamma_1 = C_1 (k_BT)^{-\alpha_1} \) with \( C_1 = 0.18(6) \) and \( \alpha_1 = 1.07(16) \). For \( T < T_g \), \( \Gamma_1 = 0.11(2) \) meV that is almost zero, independent of temperature. This contrasts with the behavior of \( \Gamma \) found in a well-known quasi-two-dimensional system \( \text{SrCt}_{9p}\text{Ga}_{12-9p}\text{O}_{19} \) where the magnetic Cr\(^{3+}\) ions form a [111] slab of a three-dimensional network of corner-sharing tetrahedra \([21]\). in SCGO, upon cooling above \( T_f \), \( \Gamma \) decreases linearly to zero at \( T_f \), but it increases back upon further cooling, which was attributed to the absence of local low-energy excitations in the frozen state.\([16]\).

The gapless short range collinear spin order observed in \( \text{Ag}_2\text{MnO}_2 \) is quite different from the ground states observed in other related materials, \( \text{Cs}_2\text{CuCl}_4 \) with gapless long range incommensurate spiral order, and \( \text{NaMnO}_2 \) with gapped long range collinear order. What determines the particular ground state in a spatially anisotropic triangular system? Spin wave analysis for varying the spatial anisotropy \( \alpha = J_f/J \) \([4]\) predicts two regions where the classical ordered state is unstable: for small \( \alpha \) where one-dimensional fluctuations become important and near \( \alpha = 1/2 \) where classically there is a transition between collinear and spiral phases. The nature of the ordered states developed by quantum fluctuations in these regions is not clear. For \( s = 1/2 \), predictions vary: a collinear magnetic state \([3]\) or a valence bond state, either gapped \([7]\) or ungapped \([11]\) separated by a quantum critical point from the spiral phase. For \( s = 2 \), there should be a quantum critical point at smaller \( \alpha \) from the Haldane gap state, as in \( s = 1 \) \([8]\), to either a collinear or a spiral state. While the microscopic origin is not yet certain, the gapless excitations and the glassiness observed in \( \text{Ag}_2\text{MnO}_2 \) suggest that the collinearity is an intrinsic property of the anisotropic triangular antiferromagnet. Multiple (three- or four-) spin exchange on the triangle, as dominates the magnetism of absorbed He\(^3\) \([22]\), might stabilize the gapless collinear structure over a wider range of parameter values \([6]\), and produce a gapless spin liquid state, as proposed for spin 1/2 \([22]\).

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* Electronic address: shlee@virginia.edu

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