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Modeling the Berezinskii-Kosterlitz-Thouless transition in $NiGa_2S_4$

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In the two-dimensional superfluidity, the proliferation of the vortices and the antivortices results in a class of phase transition, the Berezinskii-Kosterlitz-Thouless (BKT) transition. This class of phase transition is also anticipated in the two-dimensional magnetic systems. However, its existence in the real magnetic systems still remains mysterious. Here we propose a phenomenological model to illustrate that the spin-freezing transition recently uncovered in the nuclear magnetic-resonance experiment on the $NiGa_2S_4$ compound is of BKT type. The spin-freezing state observed in the $NiGa_2S_4$ possesses the power-law decayed spin correlation.

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As the thermodynamic conditions in the environment change, for example the pressure or the temperature, matter transforms from one state to another. Steam levitates from the top of the hot coffee; ice melts in the soft drink. The phase transition is ubiquitous in our daily life. Investigating the phase transition is always a central subject in physics. Most of the phase transitions can be understood by the distinct physical properties between the phases. For example, in the vapor-liquid transition, the unit volumes per mole of the molecules are different from the vapor to the liquid. In the ferromagnetic transition, the spins orientate randomly at the high-temperature side but start to align along the same direction resulting in the net magnetization at the low-temperature side. However, in the two-dimensional (2D) superfluid, the Berezinskii-Kosterlitz-Thouless (BKT) transition that happens when vortices and the antivortices proliferate does not separate the phases with distinct thermodynamic quantities.[1] Instead, the superfluidity correlation changes from the power-law behavior to the exponentially decayed one as we cross the transition from the lower-temperature side. In the two-dimensional magnetic systems, the BKT transition is also anticipated in all easy-plane Heisenberg models. On the other hand, the power-law decayed spin correlation may play an important role in the high transition temperature superconductor.[2] Therefore, understanding the spin dynamics in the critical *phase* has become tremendously important.

$NiGa_2S_4$ is originally synthesized intending to realize the spin liquid proposed by Anderson a few decades ago.[3] It is the layered material that the spin-one Ni^{2+} ions form the ideal two-dimensional triangular network. As an antiferromagnetic insulator, $NiGa_2S_4$ exhibits no long-ranged magnetic ordering down to 350 mK shown in the specific-heat capacity, the magnetic susceptibility, and the neutron-scattering experiments.[4] At 1.5 K, the Edwards-Anderson order parameter $Q=1/N\Sigma_i\langle S_i\rangle^2$ that tells the spin moment is measured at 0.61, where N is the total number of spins. This vastly reduced spin moment indicates the presence of the strong quantum fluctuation that is highly favorable by the scenario of the spin liquid. However, in the recent experiments of the Ga nuclear magnetic resonance (Ga NMR),[5] a temperature T_f is found around 10 K below which the spin dynamics slows down and the freezing behavior is observed. As approaching T_f from above, both the nuclear-spin-lattice relaxation rate $1/T_1$ and the nuclear-spin-spin relaxation rate $1/T_2$ diverge. Moreover, spins do not freeze immediately at T_f but persist fluctuating down to 2 K as found in the nuclear quadruple resonance measurement (NQR). Below 2 K, the Ga-NQR spectrum becomes very broad and featureless, which implies the formation of the *static* inhomogeneous internal magnetic field. First, intuitively, the static internal magnetic field occurs when the spins freeze up completely. In this case, the Edwards-Anderson order parameter should be close to the quantum number of the spin angular momentum. Second, all thermodynamic quantities change smoothly at the transition temperature T_f, but $1/T_1$ and $1/T_2$ diverge in the NMR signals. Therefore, the later NMR experiment apparently looks inconsistent with the previous measurements. In this Rapid Communication, we shall provide a consistent picture to compromise all the experimental results. Most importantly, we illustrate that the spin-freezing transition at $T=T_f$ is the long-sought BKT transition in the two-dimensional magnetic systems.

The way to compromise with all the experiments is to consider the state that contains both the freezing spins and the fluctuating ones. Then, both of them can be observed simultaneously in the experiments. Before explaining further, let us begin by reviewing the spin configuration [depicted in Fig. 1(a)] observed in the neutron-scattering experiment. The correlation has the wave vector (1/6, 1/6, 0) with the wavelength $2\pi/3a$, where a names the lattice constant between two Ni^{2+} ions. This wave vector simply means that along the $\mathbf{a}_1$ direction, the periodicity is of six sites and so is it along the $\mathbf{a}_2$ direction; and that along $\mathbf{b}=(1,1,0)$, the periodicity is of three sites. For convenience, we highlight the triangles in Fig. 1(a) as the reference. With respect to the reference triangles, spins have the "one-in-two-out" (one spin points in and two spins point out with respect to the triangles) or the "two-in-one-out" configurations. Inspired by the observation in the NMR experiment that the spin correlation starts to develop below the Curie-Weiss temperature of 80 K, we assume that the existence of an easy axis on every spin site and its orientation is either parallel or antiparallel to the current spin configuration. In order to manifest the antiferromagnetic nature, we assign the local $+z$ axis to be the "all in" or the "all out" with respect to the reference triangles alternating over the whole lattice. An example of the orientation of the local axes is depicted as the black thin arrows in Fig. 1(a). In this transformed coordinate, spins are either +1 (parallel to the $+z$ direction) or −1 (antiparallel to the $+z$ direction).

Considering the quantum fluctuation explicitly, we pro-

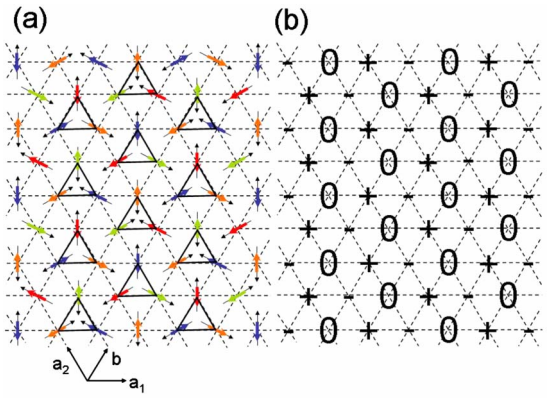

FIG. 1. (Color online) (a) The spin structure observed by the neutron scattering in Ref. 4. There are two arrows on every site. The colored one is the spin orientation, and the thin black one is the local easy axis. (b) The ground state of the antiferromagnetic quantum Ising model on the triangular lattice. "−" indicates the local "−1" state and "+" is the local "+1" state. "Zero" is the linear superposition of the "+1" and "−1" states.

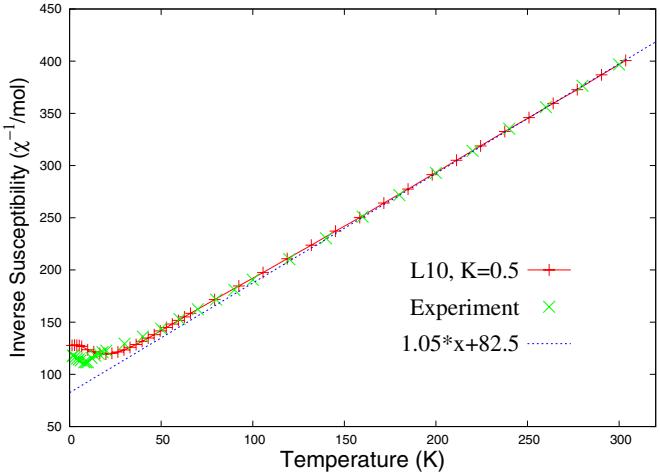

FIG. 2. (Color online) The system size is 10×10 with 100 spins in the calculation. The theoretical result has the same structure as the experiments. At the dip of χ^{-1}, marked as T_f, the spin-freezing transition occurs as found in the Ga-NMR experiments.

pose the following phenomenological Hamiltonian in the transformed coordinate:

$$H = J\sum_{\langle ij\rangle} \sigma_i^z \sigma_j^z - K\sum_i \sigma_i^x, \tag{1}$$

where σ^z take the eigenvalues +1 and −1, J is the positive phenomenological coupling constant, and K is the positive measure. Since σ^x has the off-diagonal matrix elements that connect the +1 and −1 states, K measures the spin-flipping process between the +1 and −1 states. For small K, the ground state of Eq. (1) on the triangular lattice is given in Fig. 1(b). Using our coordinate transformation, we can map the spin configuration in Fig. 1(a) to the ground state of Eq. (1). If the spin is parallel to the local $+z$ axis, we assign +1; if it is antiparallel, we assign −1. In this way, there are spins that are surrounded by the equal numbers of +1 and −1. If those spins flip, the energy from the first term in Eq. (1) does not change, but this process is encouraged by the second term. Earlier numerical calculation confirms that eventually the "zero state" is favored, which occupied +1 and −1 with an equal probability.[6,7] Then, this state with the thermal fluctuation naturally resolves the inconsistency between the experiments. The Edwards-Anderson order parameter of this state is 0.6677 (Ref. 8). It contains both the freezing and fluctuating sites. Below the freezing temperature T_f, the freezing sites contribute to the static internal magnetic field observed in the Ga-NMR experiment, and the fluctuating sites remain fluctuating down to zero temperature to contribute to the reduced moment found in the neutron scattering. We note that although the spin variable on the "+1" and "−1" sites may change with the coordinate transformation, the one on the "zero" site does not. The Edward-Anderson order parameter is invariant with respect to our coordinate transformation.

At the mean-field level, as discussed in Ref. 4, the state in Fig. 1 can be stabilized by a ferromagnetic nearest-neighbor exchange and an antiferromagnetic third-nearest-neighbor exchange. Photoemission spectroscopy also supports the enhanced contribution from the third-nearest-neighbor sites.[9] Moreover, in a high temperature, the superexchange in this material is believed to be isotropic. These complexities concerning the microscopic details are not included in this Rapid Communication. We remark that our phenomenological model is built on top of the existence of the abnormal spin correlation below the Curie-Weiss temperature. The superexchange in our model is *antiferromagnetic* in the *transformed* coordinate. Most importantly, the existence of the critical phase, as will be shown later, and the validity of the current model to describe the critical behavior help avoid those complexities. In other words, Eq. (1) might be the fix-point Hamiltonian of the fundamental microscopic model.

Now, let us focus on the spin-freezing transition observed at T_f. Since the polycrystalline sample was used in the magnetic-susceptibility measurement, we apply the quantum Monte Carlo technique to calculate the averaged susceptibility χ defined by $1/3(\chi_{xx}+\chi_{yy}+\chi_{zz})$, where $\chi_{ij}=dm_i/dh_j$, m_i is the magnetization per site, and h_j is the external magnetic field. In the calculation, the 10^6 Monte Carlo steps with the average over 64 ensembles is used. In addition, the cluster algorithm is applied along the imaginary time direction. In Fig. 2, the result of the inverse susceptibility χ^{-1} with $J=66$ K (in the temperature unit) and $K=0.5J$ is presented. It is compared qualitatively well with the experiment and shows weak size dependence because of its average nature. Both of them have the spoonlike shape that contains the dip, but the position of the dips happen at different temperatures from the theoretical result and the experimental one. We mark the temperature of the dip T_c in the theoretical result and T_f in the experimental one.

In the Ga-NMR experiments, the spin-freezing transition is observed at the dip of the inverse susceptibility, and an unusual spin correlation starts to develop at the Curie-Weiss temperature of 80 K. To understand this, we compute the spin-spin correlation along the $\mathbf{a}_1$ direction defined by

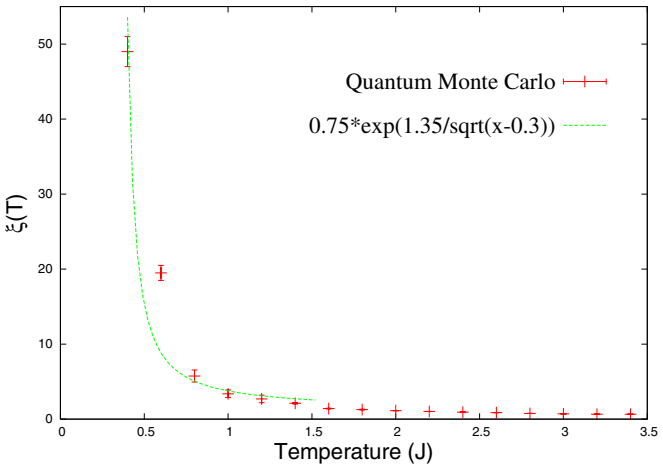

FIG. 3. (Color online) The result of $\xi(T)$. The temperature is in the unit of J, and the correlation length is in the unit of lattice constant a. At the high-temperature side of T_c ($\sim 0.3J$), the spin correlation is exponentially decayed, and the correlation length diverges at T_c. Below T_c, the phase has the power-law spin correlation. The green line is the theoretical fit of the 2D XY universality class.

$$D(n\mathbf{a}_1) = \frac{1}{N}\sum_i \langle \sigma_i^z \sigma_{i+n}^z \rangle, \tag{2}$$

in the $L_x \times M$ geometry with the periodic boundary condition. From here L_x is the length along the $\mathbf{a}_1$ direction and M is the one along the (1, 1, 0) direction, and $L_x \sim 4M$ is taken. In this case, the correlation length $\xi(T,M)$ scales with M. We define

$$\xi(T) = \lim_{M\to\infty} \xi(T,M), \tag{3}$$

and it is shown in Fig. 3. We find that the spin correlation starts to develop at $1.4J$ and it diverges at $T_c \sim 0.3J$.

At T_c, the BKT-type transition occurs. Above T_c, for example $T=0.4J$, $\xi(T,M)$ saturates exponentially as shown in Fig. 4. Below T_c, for example $T=0.2J$, $\xi(T,M)$ is linear to M. This linearity has only two possibilities: (1) the correlation length is so large that our system sizes are too small to reach the saturation; (2) it is in the critical phase. Because of the conformal invariance of the critical phase in the two dimensions, the spin correlation decays exponentially in the torus geometry. In this case, $\xi(T,M)$ is linear to M. Furthermore, the scaling dimension $\Delta(T)$ can be obtained by

$$\xi(T) = \frac{1}{2\pi\Delta(T)} M, \tag{4}$$

where Δ is defined by

$$\langle \sigma^z(0)\sigma^z(r)\rangle \sim \frac{1}{r^{2\Delta}}. \tag{5}$$

The first possibility can be ruled out as the following. In Fig. 5, we plot the initial slope of $\xi(T,M)$ defined by $\partial\xi(T,M)/\partial M|_{M=0}$. It shows a clear phase transition at $T=T_c$. If the first possibility were true, the initial slope would have been monotonic and would have grown exponentially

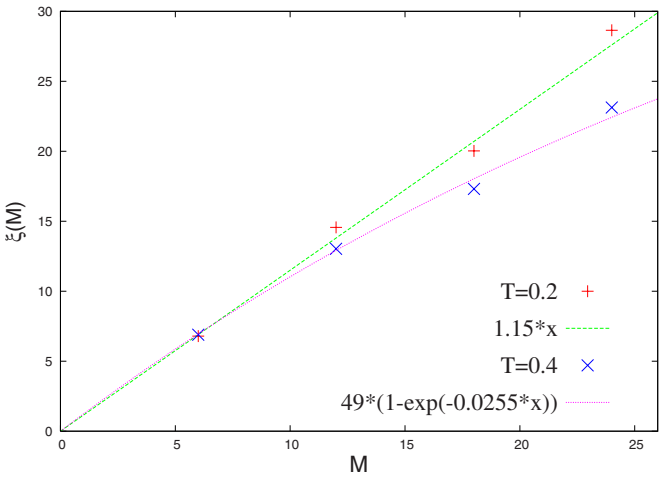

FIG. 4. (Color online) $\xi(T,M)$ at $T=0.2J$ and $0.4J$. The vertical axis is $\xi(T,M)$, and M is in the unit of the lattice constant a. At $T=0.4J$, the correlation length saturates exponentially. At $T=0.2J$, the linear scaling implies the critical phase as explained in the text. The two lines are the functional fit to the data.

as temperature decreases. However, the slope has a discontinuity at T_c, indicating a phase transition. Moreover, it is not a second-order phase transition, because both the magnetic susceptibility and the specific heat are smooth functions at T_c. If it is a classical Ising transition, $\xi(T)$ should be symmetric with respect to T_c as $|T-T_c| \ll 1$. Here, although the initial slopes at $T=0.2J$ and $T=0.4J$ are the same within the error bar, their asymptotic behaviors are entirely different as shown in Fig. 4. Therefore, the phase below T_c should be critical with the power-law spin correlation. Additionally, the scaling dimension $\Delta(T)$ has the monotonic temperature dependence, which is the typical behavior of the scaling dimension in the critical phase. Due to the restriction of the technique, we are not able to compute the free energy to find the central charge in the critical phase. Classification by the con-

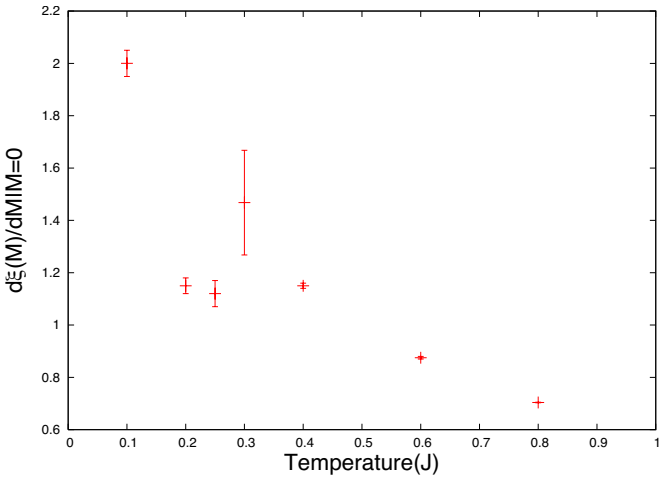

FIG. 5. (Color online) The temperature is in the unit of J. The vertical axis is the initial slope of $\xi(T,M)$ defined in the text. If there is no phase transition, the initial slope should be exponentially and monotonically increasing. However, there is a discontinuity at $T=0.3J$, which indicates a phase transition.

formal field theory may be an interesting direction for future research.

The existence of the BKT transition in the quantum Ising model on the triangular lattice was previously pointed out by Moessner *et al.*[7] Here we summarize their argument and further construct the topological object in this model. The quantum 2D model of Eq. (1) at finite temperature can be mapped to a three-dimensional (3D) classical Ising model with the ferromagnetic exchange along the imaginary time direction with *finite dimension*. Using the Landau-Ginzburg-Wilson analysis, the 3D model can be mapped to an XY model with a sixth-order symmetric breaking term, which has the sixfold clock symmetry. At zero temperature, there is a quantum phase transition described by the 3D XY universality class at finite K, because the clock term is dangerously irrelevant in 3D. However, at *finite* temperature and in the thermodynamic limit, the 3D model crosses over to the 2D model and it results in two transitions: one is BKT transition at higher temperature and the other at lower temperature that corresponds to the sixfold clock symmetry breaking, for example, to the state in Fig. 1(b). Therefore, the BKT transition in $NiGa_2S_4$ actually belongs to the 2D XY universality class. In Fig. 3, we fit the correlation result well with the 2D XY model.[10] These two transitions are both seen in the Ga-NMR experiment.[5] The spin-freezing transition at 10 K is the BKT transition, and the transition at 2 K where spins completely freeze up corresponds to the second transition.

It is not coincident that the phase transition occurs at the dip of χ^{-1}. Once the power-law spin correlation survives in the *phase* rather than a critical point, the response to the external field could be weaker. Due to the slow spin dynamics, the magnetic susceptibility begins to drop in the critical phase.

In Fig. 6, we show the calculation of the specific-heat capacity. It illustrates the double-peak structure and the reason is similar to the one given in Ref. 11, although the valley between the peaks is not as deep as the experimental one shown in Ref. 4. The magnetic specific heat in Ref. 4 is obtained by subtracting the specific heat of $ZnIn_2S_4$, which is nonmagnetic and isostructural to $NiGa_2S_4$, from the one of the $NiGa_2S_4$. We remark that there is 29.68% difference in the total atomic mass between these two compounds. How reliable their magnetic specific result is suspicious to us. However, their low-temperature result may be correct. Here we also find no evidence of the existence of the energy gap, which is consistent with their experiment.

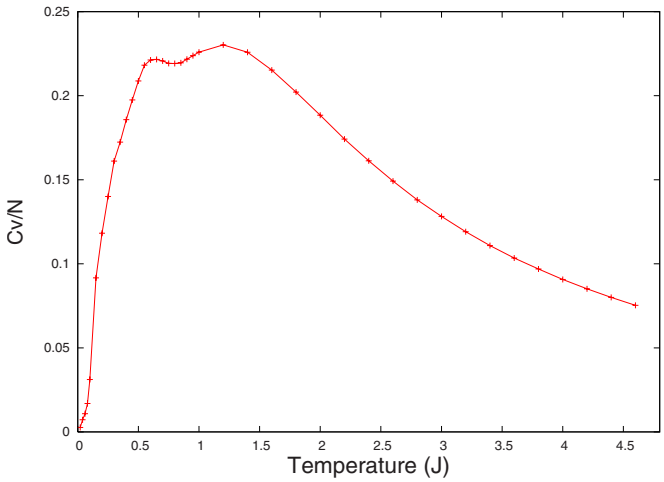

FIG. 6. (Color online) The temperature dependence of the specific-heat capacity. The temperature is in Kelvin.

In summary, we have shown that the spin-freezing transition seen in the Ga-NMR experiment on the $NiGa_2S_4$ compound is the BKT-type transition, which belongs to the 2D XY universality class. The divergence of the spin correlation leads to the divergence of $1/T_1$ and $1/T_2$. Below T_f, the power-law spin correlation develops in the state in Fig. 1. The truly long-ranged spin correlation happens at the zero temperature and dubbed by the "order by disorder."[6,7] Through our analysis, $NiGa_2S_4$ should be removed from the candidate list for the spin-liquid ground state. Finally, the long-sought BKT transition in the quantum spin system is unexpectedly found. The phase accompanying the phase transition will refresh our understanding of the spin dynamics in the critical phase.

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