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Nonmonotonic field dependence of the Néel temperature in the quasi-two-dimensional magnet $[Cu(HF_2)(pyz)_2]BF_4$

P. Sengupta,[1,2] C. D. Batista,[1] R. D. McDonald,[2] S. Cox,[2] J. Singleton,[2] L. Huang,[3] T. P. Papageorgiou,[3] O. Ignatchik,[3] T. Herrmannsdörfer,[3] J. L. Manson,[4] J. A. Schlueter,[5] K. A. Funk,[5] and J. Wosnitza[3]

[1]*Theoretical Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA*

[2]*MPA-NHMFL, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA*

[3]*Hochfeld-Magnetlabor Dresden (HLD), Forschungszentrum Dresden-Rossendorf, P.O. Box 510119, D-01314 Dresden, Germany*

[4]*Department of Chemistry and Biochemistry, Eastern Washington University, Cheney, Washington 99004, USA*

[5]*Materials Science Division, Argonne National Laboratory, Argonne, Illinois 60439, USA*

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The measured thermodynamic phase diagram of the quasi-two-dimensional magnet $[Cu(HF_2)(pyz)_2]BF_4$ (pyz=pyrazine=$N_2C_4H_4$) exhibits an unusual nonmonotonic dependence of the Néel temperature T_N as a function of magnetic field H. The nonmonotonic behavior of $T_N(H)$ results from two competing effects induced by the field: while H suppresses the amplitude of the order parameter by polarizing the spins along a given direction, it also reduces the phase fluctuations by changing the order parameter space from the sphere S^2 to the circle S^1. The latter effect dominates at low fields only if the system is close enough to its lower critical dimension ($d_c=2$), i.e., when fluctuations become important. Our theoretical results reproduce the measured phase diagram and demonstrate that this unusual effect is realized in $[Cu(HF_2)(pyz)_2]BF_4$.

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In a mean-field treatment, interacting systems are described by a single-particle Hamiltonian that results from taking the average of the fluctuating field produced by the other particles. Since the interactions are usually short-ranged, the average field is generated by the neighboring particles. For lattice systems, the number of neighbors is just the coordination number z. When this number increases, the field fluctuations average out and become small relative to the mean-field value. Indeed, this is why mean-field approaches work well in systems with higher dimensionality (large z). However, field fluctuations become important in systems with reduced dimensionality and can introduce qualitative changes. A simple example of such qualitative change is the lack of ordering at finite temperature below a lower critical dimension d_c.

The possibility of observing different and sometimes counterintuitive behaviors induced by strong fluctuations makes systems with reduced dimensionality attractive subjects for research. Unfortunately, such systems are not abundant in nature. Compounds are three dimensional in general although interactions can be highly anisotropic making them quasi-one-dimensional or quasi-two-dimensional. Sufficiently high anisotropy often enables anomalous behaviors induced by strong fluctuations to be observed in these systems. This is the case for $[Cu(HF_2)(pyz)_2]BF_4$, a compound whose structure contains a tetragonal lattice of $S=1/2$ spins and whose magnetic properties are very well described by a nearest-neighbor antiferromagnetic Heisenberg model. The intralayer exchange interactions are estimated from uniform susceptibility measurements as $J_a=J_b=5.9$ K (Ref. 1). We used the measured Néel temperature in zero field[2] and its known dependence on the interlayer exchange to obtain $J_c \simeq 0.015$ K.[3]

It is well known that pure two-dimensional (2D) magnets with uniaxial anisotropy such as the ones described by an *XY* model undergo a Berezinskii-Kosterlitz-Thouless (BKT) transition[4,5] at a finite temperature T_{BKT}. The high-temperature disordered phase with exponentially decaying spin-spin correlations consists of a gas of vortices. The energy of a vortex is finite and proportional to $\ln L/a_0$, where a_0 is of the order of the lattice parameter and L is the linear system size. At temperatures $T<T_{BKT}$, the vortices are bound in pairs leading to a critical spin state: the spin-spin correlation function decays algebraically with distance and the spin stiffness is nonzero. The situation is qualitatively different for 2D isotropic Heisenberg magnets.[5,6] In this case, the spin is free to point in any direction and the metastable vortex defect of the anisotropic case is replaced by a texture called meron[7] in which the spins near the center are tilted out of the *xy* plane to acquire a finite *z* component. In this way, the new texture avoids the singular behavior that appears in the center of a vortex, i.e., the spin is a smooth function of position. The energy of this texture is proportional to $J_{\parallel} \ln(L/\xi_0)$, where ξ_0 is the linear size of the tilted region and $J_{\parallel}$ is the exchange constant in the *xy* plane ($J_{a,b}$). In particular, a meron-antimeron pair with opposite spins forms a texture called skyrmion[7] that has a finite energy in this isotropic limit. The skyrmions proliferate at any finite temperature due to the energy-entropy balance. This explains the absence of a finite-temperature phase transition ($T_{BKT}=0$) for the isotropic 2D Heisenberg model.[8]

The application of a magnetic field, H, to a 2D Heisenberg antiferromagnet offers the possibility of observing a continuous transition between the uniaxial and isotropic cases discussed in the previous paragraph. The system is isotropic for $H=0$, meaning that there is no BKT transition: $T_{BKT}(H=0)=0$. For finite H, the antiferromagnet only has uniaxial symmetry and the staggered spin component (order parameter) is parallel to the *xy* plane if H is along the z direction. In this situation, ξ_0 cannot increase indefinitely because there is an energy cost for tilting the order parameter out of the *xy* plane: $\delta E \propto H^2 \xi_0^2 / J_{\parallel}$. Since the energy gain is proportional to $J_{\parallel}[\ln(L/\xi_0)-\ln(L/a_0)]$, we obtain an optimal value of $\xi_0 \propto |J_{\parallel}/H|$.[9,10] Consequently, the linear size of the vortex core remains finite for nonzero fields, leading to a finite value of T_{BKT} for $0<|H|<H_{\mathrm{sat}}$, where H_{sat} is the saturation field.

The asymptotic ($H\to 0$) field dependence of T_{BKT} can be determined by using the following argument. When approaching the BKT transition from the high-temperature (disordered) region, the antiferromagnetic correlation length has the temperature dependence of the isotropic point close enough to $H=0$: $\xi_{\mathrm{AFM}}(T)\propto e^{2\pi\rho_s/T}$,[11,12] where ρ_s is the spin stiffness. The anisotropy introduced by the magnetic field becomes relevant when the correlation length, ξ_{AFM}, becomes comparable to the linear size of the vortex core ξ_0. This occurs at a characteristic temperature T_0 defined by $\xi_{\mathrm{AFM}}(T_0)\sim\xi_0$, which leads to $T_0 \propto J_{\parallel}/\ln|J_{\parallel}/H|$. For temperatures significantly lower than T_0, the system behaves like a pure XY magnet and must exhibit quasi-long-range order. This implies that T_{BKT} and T_0 correspond to the same energy scale: $T_{\mathrm{BKT}}\propto T_0 \propto J/\ln|J/H|$, i.e., T_{BKT} decreases very abruptly to 0 for $|H|\to 0$ (Ref. 13). A more formal derivation of this logarithmic dependence can be found in Ref. 14.

Unfortunately, the interlayer coupling $J_{\perp}$ is a relevant variable that always exists in real compounds and changes the pure 2D picture in a qualitative fashion. As long as this coupling is finite, the system undergoes a second-order phase transition for any value of H and the finite-temperature critical properties of the 2D system are lost. This is the reason why it is very difficult to observe BKT transitions in real magnets. In addition, the zero-field ordering temperature increases very rapidly with the interlayer coupling:[15,16] $T_N(H=0)\propto -J_{\parallel}/\ln\gamma$ for small $\gamma(\equiv J_{\perp}/J_{\parallel})$. However, one of the unusual qualitative phenomena of pure 2D magnets is not lost, as long as the interlayer coupling is small enough. This is the nonmonotonic field dependence of the critical temperature. For finite $J_{\perp}$, the sharp minimum of $T_{\mathrm{BKT}}(H)$ at $H=0$ is replaced by a smooth behavior of the critical temperature $T_N(H)$. The minimum at $H=0$ persists as long as the anisotropy ratio, γ, is small enough. Since $T_N(H=0)$ increases very rapidly with γ, a highly anisotropic magnet is required to still observe the nonmonotonic behavior of $T_N(H)$. The primary aim of this Rapid Communication is to demonstrate that such behavior is indeed observed in the highly anisotropic quasi-2D magnet $[\mathrm{Cu(HF_2)(pyz)_2}]\mathrm{BF_4}$.

The strongly 2D nature of $[\mathrm{Cu(HF_2)(pyz)_2}]\mathrm{BF_4}$ can be rationalized by its crystal structure[1] (see Fig. 1). Each Cu(II) ion is linked into a 2D square lattice (in the ab plane) by organic pyrazine ligands (Cu-Cu distance=6.852 Å) as shown in Fig. 1. The sheets are connected along the c axis by $\mathrm{HF_2^-}$ ligands (Cu-Cu distance=6.619 Å) to generate a 3D tetragonal lattice. Due to the similar metal-metal distances this material may be deemed an anisotropic cubic lattice. By considering the orientation of the magnetic $d_{x^2-y^2}$ orbital that occupies the ab plane and directly overlaps with ligand orbitals of the pyrazine ligand, the system should behave as a two-dimensional magnet. Indeed, long-range magnetic order occurs below 1.63 K as detected by muon-spin relaxation measurements.[1] The fact that T_N is significantly reduced compared to the energy of the exchange interaction points to a low-dimensional magnetic character.

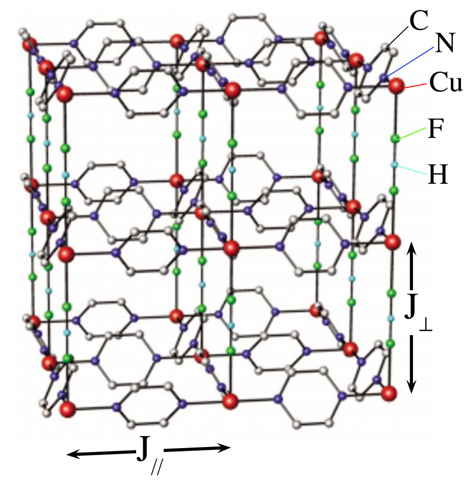

FIG. 1. (Color online) Crystal structure of $[\mathrm{Cu(HF_2)(pyz)_2}]\mathrm{BF_4}$. Hydrogen atoms on the pyrazine rings and interstitial $\mathrm{BF_4}$ anions have been omitted for clarity.

The magnetic properties of $[\mathrm{Cu(HF_2)(pyz)_2}]\mathrm{BF_4}$ are well described by a Heisenberg model on a tetragonal lattice,

$$\mathcal{H}=J_{\parallel}\sum_{\langle i,j\rangle_{xy}}\mathbf{S}_i\cdot\mathbf{S}_j+J_{\perp}\sum_{\langle i,j\rangle_z}\mathbf{S}_i\cdot\mathbf{S}_j-h\sum_i S_i^z, \tag{1}$$

where $J_{\parallel}$ and $J_{\perp}$ are the intra- and interlayer exchange constants estimated as $J_{\parallel}=J_{a,b}=5.9$ K (Ref. 1) and $J_{\perp}=J_c \simeq 0.015$ K from measured T_N at $H=0$.[2,3] This corresponds to an anisotropy ratio $\gamma\approx 1/400$. $\langle i,j\rangle_{xy}$ and $\langle i,j\rangle_z$ denote nearest-neighbor pairs parallel and perpendicular to the layers. $h=g\mu_B B$, where the magnetic induction B is related to the applied field as $B\simeq\mu_0 H$ (valid for systems with small susceptibilities). The gyromagnetic factor g is estimated from spectroscopic methods as $g=2.13$.

We have used the stochastic series expansion (SSE) quantum Monte Carlo method[17] to study the thermal phase transition of the model (1) as a function of the external field H. For comparison, we computed the field dependence of T_{BKT} for $J_{\perp}=0$, i.e., the Heisenberg model on a square lattice (see Fig. 2). On the dense temperature grids needed to study the

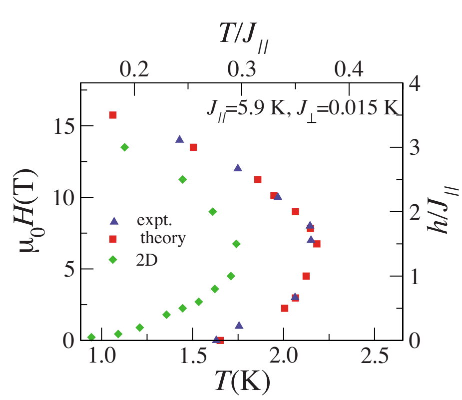

FIG. 2. (Color online) The nonmonotonic field dependence of the ordering temperature of $[\mathrm{Cu(HF_2)(pyz)_2}]\mathrm{BF_4}$ as determined from specific-heat data and as predicted from model (1). For comparison, the results for the pure 2D case ($J_{\perp}=0$) are also shown.

critical region in detail, the statistics of the Monte Carlo results can be significantly improved by the use of a tempering scheme.[18,19] The implementation of tempering schemes in the context of the SSE method has been discussed in detail previously.[15,20] Here we follow the thermal parallel tempering scheme developed in Ref. 15.

An efficient way to determine the transition temperature is to exploit the scaling properties of the spin stiffness. The stiffness is defined as the second derivative of the free energy with respect to a uniform twist ϕ (Refs. 21 and 22): $\rho = \frac{\partial^2 F(\phi)}{\partial \phi^2}$, and it is related to the fluctuations of the "winding number."[17,23,24] Hence, it can be estimated directly in the SSE simulations by working in the grand canonical ensemble. Since the twist can be applied parallel or perpendicular to the planes, there are two different spin stiffnesses, ρ_x and ρ_z, for the anisotropic system considered here.

We use the finite-size and temperature dependence of the spin stiffnesses to determine the critical temperature.[15,17,25] For a fixed aspect ratio, the stiffness at T_c scales as $\rho_\mu = L_\mu^{2-d}$, $\mu = x,z$, where d is the dimensionality of the system. This implies that for the 3D Heisenberg model, on a plot of $L_\mu \rho_\mu$ as a function of T the curves for different system sizes will cross each other at T_c. We studied tetragonal lattices $(L_x = L_y \neq L_z)$ (Ref. 26) with $16 \leq L_x \leq 128$ and a fixed aspect ratio $L_x/L_z = 4$ to obtain the Néel temperature over a range of magnetic fields $0 \leq h/J_\parallel < 4.0$. For the 2D model, we used square lattices and the same range of field.

A comparison between simulation and experiment provides a quantitative confirmation of the nature of thermal transition in $[Cu(HF_2)(pyz)_2]BF_4$ (Fig. 2). The experimental data were obtained from high-resolution specific-heat measurements of a single crystal sample.[2] At zero field, the pure 2D model is disordered for all $T > 0$, but the weak interlayer coupling in the real material ($J_c \simeq 0.015$ K) leads to long-range AFM order below $T_N = 1.63$ K—a consequence of the extremely rapid increase in the ordering temperature with interlayer coupling, $T_N \propto -J_\parallel/\ln(\gamma)$. However, this ordering temperature ($T_N/J_\parallel = 0.276$) is greatly reduced from its value in the isotropic ($\gamma = 1$) limit ($T_N/J \approx 0.96$), implying a highly two-dimensional character. The vortex structures of the 2D model are still the primary low-lying excitations that destroy the long-range order above T_N and the consequent nonmonotonic field dependence of the ordering temperature is expected to hold given the small value of $\gamma = 1/400$. Indeed, as it is shown in Fig. 2, the simulation results for the model Hamiltonian $\mathcal{H}$ [Eq. (1)] closely follow the observed behavior. The excellent agreement between the theoretical prediction and the experimental data over the entire range of the applied field confirms that the thermal transition in $[Cu(HF_2)(pyz)_2]BF_4$ exhibits characteristics of pure 2D magnets.

Having determined T_N as a function of $\mu_0 H$, we now present the results for the temperature dependence of the specific heat at different field values. The specific heat is defined as the temperature derivative of the energy, $C = (\partial E/\partial T)/N$ (N is the system size). The SSE method allows us to obtain a direct estimate of C from the operator sequence in the simulation, $NC = \langle n^2 \rangle - \langle n \rangle^2 - \langle n \rangle$, where n is the power-series expansion order which fluctuates in the simulations.[15] In principle, this avoids additional noise due to numerical differentiation of the energy function. In practice, the noise due to numerical differentiation of the energy is sufficiently small so that both approaches work equally well.

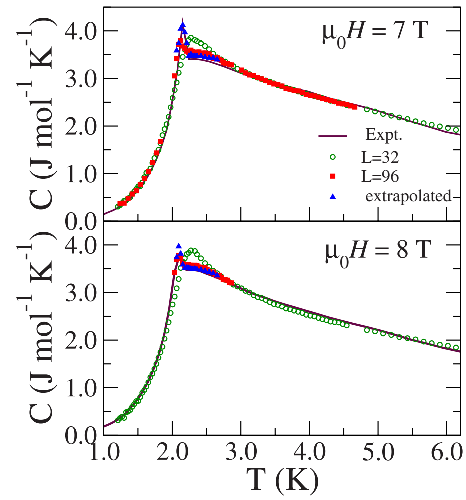

FIG. 3. (Color online) The measured (solid line) and calculated (symbols) heat capacity for two values of the magnetic field. The excellent agreement between the experimental data and simulation results over the entire range of temperature—including the position and amplitude of the peak—without any adjustable parameter further validates model (1) used to describe the magnetic properties of $[Cu(HF_2)(pyz)_2]BF_4$.

In absence of an applied field, the specific heat for the 3D Heisenberg model on highly anisotropic lattices ($\gamma \ll 1$) has two separate peaks. The broad peak that appears at higher temperature originates from 2D spin fluctuations. Therefore, this is the only peak that survives in the pure 2D limit ($\gamma = 0$) and reaches its maximum value at $T \approx 0.7J$.[27] This broad maximum remains the dominant feature of the specific-heat curve for small values of γ, but a second and much sharper peak appears at $T = T_N$ indicating a phase transition to an antiferromagnetically ordered state for $T < T_N$. The amplitude of the second peak is greatly suppressed which indicates that substantial spin correlations develop in the planes before the eventual 3D transition occurs. The reduction in the size of the specific-heat anomaly makes the experimental and numerical detection of the transition more challenging for highly anisotropic systems.

T_N increases with field for $\mu_0 H \lesssim 8$ T. The entropy associated with the 3D ordering also increases with an accompanying increase in the amplitude of the specific-heat anomaly. We consider two values of the applied field close to the maximum ordering temperature ($\mu_0 H = 7$ and 8 T). The experimental data reveal a sharp peak immediately followed by a broad shoulder. These data together with the simulation results are shown in Fig. 3. Away from the critical region, the numerical data converge rapidly with system size, but close to the transition temperature, significant finite-size effects are observed. For smaller system sizes, there is a single broad peak and much larger system sizes are needed to resolve the closely spaced specific-heat anomaly and the broad shoulder. Additionally, the sharp peak is greatly rounded due to the proximity to the broad shoulder. To get the correct thermodynamic estimate, we performed a careful finite-size scaling of the specific-heat data in the vicinity of the critical temperature. The extrapolated data are found to be in excellent agreement with the experimental data over the entire range of temperature—including the position and amplitude of the peak—without the need for any adjustable parameter.

In conclusion, the large anisotropy between the inter- and intralayer exchange couplings of $[Cu(HF_2)(pyz)_2]BF_4$ results in a predominantly 2D character. The thermal transition out of the ordered state is driven by strong phase fluctuations characteristic of a quasi-2D system. This leads to an unusual nonmonotonic field dependence of the ordering temperature. The magnetic field reduces both the magnitude of the order parameter as well as the amplitude of the phase fluctuations. The latter effect is more important at low fields because, in the 2D limit, phase fluctuations are responsible for the complete suppression of long-range ordering at finite T. The suppression of the amplitude of the order parameter becomes the dominant effect at higher fields and eventually drives the Néel temperature to zero at the critical field $h_c=4J_{\parallel}+2J_{\perp}$. A straightforward mean-field theory that ignores the phase fluctuations misses the nonmonotonic behavior, predicting instead a monotonic decrease of T_N with field. Using qualitative arguments based on low-lying excitations of 2D systems and large-scale numerical simulations, we have shown that the nonmonotonic field dependence of T_N observed in $[Cu(HF_2)(pyz)_2]BF_4$ is a manifestation of its quasi-2D character. The same arguments are sufficient to explain similar behavior in other quasi-low-dimensional systems.[28,29]

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