Field-induced anisotropy in the quasi-two-dimensional weakly anisotropic antiferromagnet $[CuCl(pyz)_2]BF_4$

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We measured NMR and magnetic susceptibility for the quasi-two-dimensional, weakly XY-like, spin-1/2 square-lattice Heisenberg antiferromagnet $[CuCl(pyz)_2]BF_4$ (pyz = pyrazine = $N_2C_4H_4$) near the critical temperature. The Néel temperature T_N and the order-parameter critical exponent β were obtained from the NMR line broadening as a function of temperature. As the applied field strength ($H \parallel c$) was increased, T_N increased and β decreased. This behavior indicates that the field effectively enhanced XY anisotropy. The susceptibility as a function of temperature did not show a clear feature for T_N, but showed field-dependent minima below T_N for both $H \parallel c$ and $H \parallel ab$, where minimum features disappeared for $\mu_0 H > 2\,\mathrm{T}$.

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I. INTRODUCTION

Quasi-two-dimensional (2D) spin-1/2 square-lattice Heisenberg antiferromagnets have been widely studied because of relatively easy theoretical access and the relation with the superconducting mechanism of high-T_c cuprates [1,2]. Although strictly 2D isotropic Heisenberg antiferromagnets show no phase transition at a finite temperature [3], real magnetic materials of layered structures undergo phase transitions due to the couplings between the layers [4–8], the anisotropy in the intraplane exchange interaction [9–11], and their interplay [12–15]. The exchange anisotropy is very effective in reducing thermal and quantum fluctuations to induce transitions in 2D. For instance, for Ising-like anisotropy as weak as 1%, the Néel transition temperature T_N becomes higher than $0.2J/k_B$, where J is the intraplane exchange interaction strength [9].

The exchange anisotropy induces not only a phase transition but also a crossover [10,12–14,16]. For instance, the susceptibility minimum as a function of temperature indicates the crossover from Heisenberg to XY (Ising) anisotropy for a magnetic field applied perpendicular to the easy plane (axis) [9]. This behavior has been observed in $Sr_2CuO_2Cl_2$ [17] and Cu pyrazine compounds [13,16], and confirmed by quantum Monte Carlo (QMC) simulations [9,10,18]. The NMR spin-lattice relaxation rate reflecting the spin-spin correlations also changes its behavior across the crossover temperature T_{CO} where the susceptibility minimum occurs [12]. The crossover would take place when the thermal fluctuation energy becomes comparable to the anisotropy of the exchange interaction.

An externally applied magnetic field H is the third factor affecting the transition: The effective field-induced anisotropy reduces fluctuations, and thus increases T_N [16,18–20]. It could also give rise to a crossover from Heisenberg to XY, or from XY to Ising behavior [16,18]. In a weakly XY-like antiferromagnet, a magnetic field parallel to the z axis enhances the XY anisotropy, while the field parallel to the x axis makes that axis the hard one to produce easy axis anisotropy along the y-axis direction.

The quasi-2D Heisenberg antiferromagnet with the exchange anisotropy is described by the Hamlitonian

$$\mathcal{H} = J\sum_{nn}\left[S_i^x S_j^x + S_i^y S_j^y + (1-\Delta)S_i^z S_j^z\right] + J'\sum_{i,i'}\vec{S}_i\cdot\vec{S}_{i'} - g\mu_B\mu_0\vec{H}\cdot\sum_j\vec{S}_j, \quad (1)$$

where J' is interplane exchange interaction strength and Δ the exchange anisotropy parameter. The condition $0 < J' \ll J$ holds for the quasi-2D antiferromagnets, and $0 < \Delta \ll 1$ for the weakly XY-like interaction. Organic molecular-based antiferromagnets have been a good test bed to study 2D spin systems because J, J', and Δ can be controlled with various ligands or anions [6,21,22]. Another advantage of these compounds is the small energy scale of the exchange interactions, which makes it easy using laboratory magnets to reach a saturation field or to control the anisotropy by generating effective field-induced anisotropy Δ_H larger than the intrinsic anisotropy.

In the widely known family of $[CuX(pyz)_2]Y$ compounds [5,6,15,19,20,23–27], Cu^{2+} ($S = 1/2$) spins connected via pyrazine (pyz = $N_2C_4H_4$) molecules form square-lattice planes in a tetragonal structure. The planes are connected by X ligands in a perpendicular direction (along c axis) and charge is balanced by Y anions. Among the family, $[CuCl(pyz)_2]BF_4$ with distinctively shorter interlayer distances were recently

grown into a single crystal and extensively characterized by various experimental techniques and theoretical calculations [27]. From the model fitting to the magnetic susceptibility, J/k_B was estimated to be 9.4(1) K. Powder neutron diffraction confirmed that a simple staggered, long range magnetic order sets in below $T_N = 3.9(1)$ K, where the ordered moments lie in the *ab* plane. It is worth noting that $[CuCl(pyz)_2]BF_4$ may realize a relatively little explored case $J'/J > \Delta$ among the reported $[Cu(pyz)_2]^{2+}$ compounds [5,6,15,19,20,23–26], which, along with the applied field, may impact the critical properties.

In this paper, we report the evolution of the critical properties of $[CuCl(pyz)_2]BF_4$ with an applied magnetic field. We performed complementary NMR spectrum and dc susceptibility measurements, where the former is sensitive to the development of the transverse ordered moments and the latter probes the induced longitudinal magnetization. From the NMR measurements, we show that T_N increases and the order-parameter critical exponent β decreases as H increases. In addition, we show that the susceptibility as a function of temperature has a minimum which disappears in high fields. We discuss the results in light of the field-induced anisotropy.

II. EXPERIMENTAL DETAILS

Single crystalline $[CuCl(pyz)_2]BF_4$ samples were synthesized from the aqueous solution of $CuCl_2$, $Ag(BF_4)$, and pyrazine. The detailed synthesis method is described in Ref. [27]. Susceptibility of a sample with mass of 1.9 mg was measured using a magnetic properties measurement system (MPMS, Quantum Design, Inc.) in the temperature range from 1.8 to 8 K. Magnetic field was applied in two different directions, $H \parallel c$ and $H \parallel ab$, in the range from 5 mT to 7 T. Isothermal magnetization as a function of field was also measured at 1.8 K for $H \parallel ab$. ^{1}H NMR was measured using a homemade spectrometer and a 7 T superconducting magnet. A full spectrum was obtained by adding up the Fourier transformed spectra of Hahn echo signals measured at every 0.5 MHz. The NMR signal was recorded near the zero-field $T_N = 3.9$ K [27], from 3.10 to 4.25 K, for applied magnetic fields from 2 to 7 T.

III. RESULTS AND DISCUSSION

Figure 1 shows temperature evolution of ^{1}H NMR spectrum of $[CuCl(pyz)_2]BF_4$ at 7 T. At high temperatures above T_N, a single peak is observed, where all the hydrogen atoms are in the identical magnetic environment in a paramagnetic state. The Gaussian line shape and width above T_N remains the same up to the liquid nitrogen temperature. As temperature is lowered below 4.15 K, however, the NMR line broadens abruptly. This is due to the dipolar fields from the neighboring Cu^{2+} spins that start to order near this temperature [28]. At the lowest temperatures, the spectra consist of two peaks at both high and low frequency ends and a rather featureless, continuous intensity distribution between them. The two peaks correspond to the simple antiferromagnetic order seen by the nuclei with the largest hyperfine coupling. The continuous distribution reflects the overlapping lines from the remaining maximum 15 inequivalent sites of ^{1}H in a unit cell.

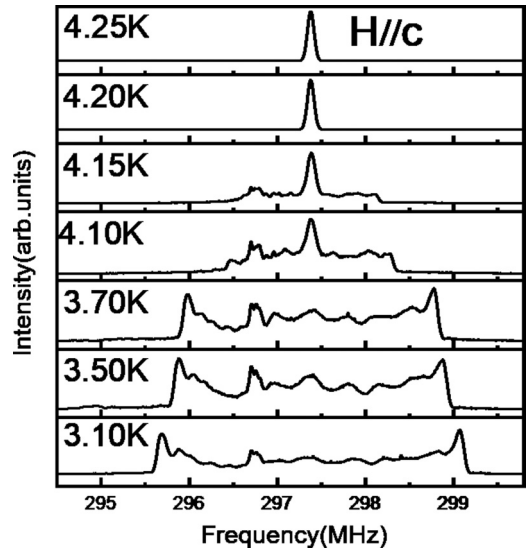

FIG. 1. ^{1}H NMR spectra of $CuCl(pyz)_2BF_4$ single crystal at different temperatures in 7 T ($H \parallel c$).

Figure 2 shows the line width δf versus temperature for different H, where δf was defined as the full width at 10% maximum. The line width is proportional to the dipole field strength at the ^{1}H sites, which is in turn proportional to the size of the ordered Cu^{2+} spin moments. Thus the data in Fig. 2 correspond to the order parameter (staggered magnetization) curve. The line widths for different fields would saturate toward the same value at sufficiently low temperature as long as the field is not disruptive to the ground state. The line widths in Fig. 2 do not reach saturation down to the lowest measured temperature, but the curves for different fields except 2 T approach each other. The shape of the curves and T_N vary, depending on the applied field strength.

Solid lines in Fig. 2 are fit to $\delta f - \delta f_0 \propto (1 - T/T_N)^\beta$, where the constant term δf_0 is the finite line width in the paramagnetic state. T_N and β were obtained from the fit, following the procedure described in Ref. [14], and plotted in Figs. 3(a) and 3(b), respectively. For each field, the whole measured temperature range was used for the fitting as

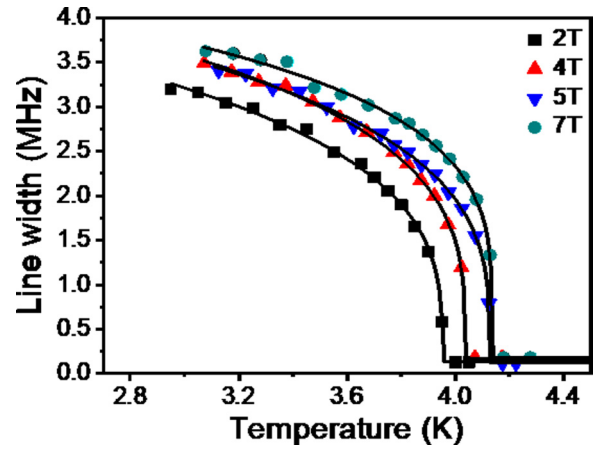

FIG. 2. NMR line width versus temperature for $H \parallel c$, where the solid lines are the best fit results (see text).

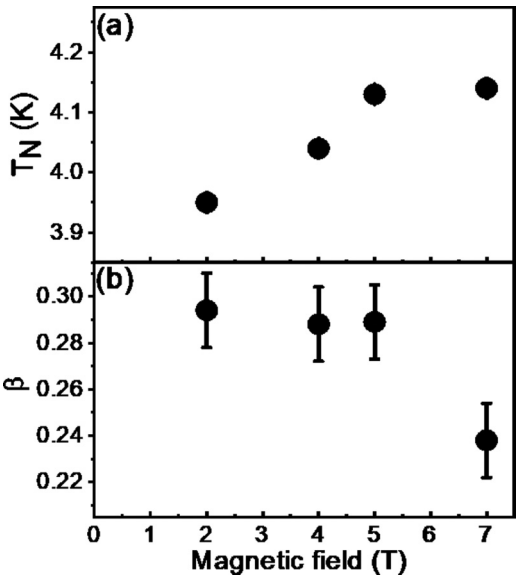

FIG. 3. (a) The critical temperature T_N and (b) the critical exponent β versus magnetic field for $H \parallel c$.

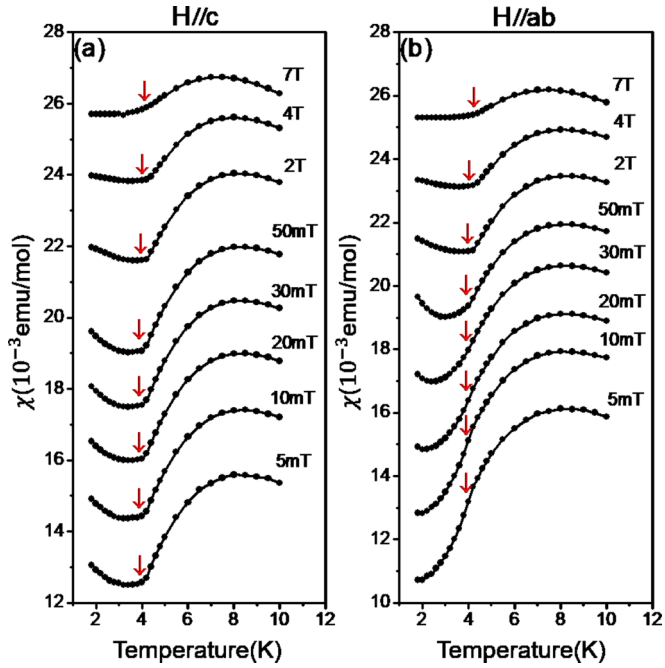

FIG. 4. Susceptibility as a function of temperature at various magnetic fields for (a) $H \parallel c$ and (b) $H \parallel ab$. The curves (except for 5 mT) were vertically shifted for better visibility. The arrows indicate T_N.

commonly practiced for the quasi-2D antiferromagnets due to a large critical region [6]. We also tried a more restrictive temperature window for the fitting, e.g., $T > 0.8T_N$, but the obtained values fall within the error bar in Fig. 3.

As shown in Fig. 3(a), T_N increases with increasing H, which is consistent with the QMC simulation of Heisenberg antiferromagnets in a magnetic field [19]. In this simulation, on increasing H, $T_N(H)$ initially increases, reaches a maximum, and then decreases following a parabolic form. The initial increase in T_N results from the field-induced XY anisotropy that reduces fluctuations. This effective field-induced XY anisotropy comes from the antiferromagnetic J, which together with the uniform field leads to canting of moments away from a plane perpendicular to the field. T_N then decreases when H becomes strong enough to disturb antiferromagnetic spin alignment. The maximal point H_m approximately satisfies the condition $g\mu_B\mu_0 H/J \sim 1.5$ [19], which gives $\mu_0 H_m \sim 10\,\mathrm{T}$ for $[CuCl(pyz)_2]BF_4$. This is consistent with the monotonic increase in T_N with the field up to 7 T shown in Fig. 3(a). Similar behavior was also observed in other Cu pyrazine compounds [16,19,20,29].

The exponent β, plotted in Fig. 3(b), monotonically decreases as H increases, from $\beta = 0.294(16)$ for 2 T to $\beta = 0.238(16)$ for 7 T. For other reported quasi-2D materials, β has been largely found between $\beta = 1/8$ of 2D Ising model and 0.23 of 2D XY model even in low fields [11,30]. The large β observed in low fields may reflect relatively strong interlayer coupling, though clear correlation between them is yet to be established [6]. The decreasing β with increasing H could be due to enhanced effective spin anisotropy similar to the $T_N(H)$ case. The field-induced anisotropy at 7 T is estimated [18] to be $\Delta_H \sim 0.1(g\mu_B\mu_0 H/JS)^2 \sim 0.4$, which is much larger than the expected Δ. The Cu^{2+} g-values of $[CuCl(pyz)_2]BF_4$ are 2.06 and 2.27 for a and c directions, respectively [27], which are the typical values when the angular momentum of the Cu ions located at noncubic sites is not perfectly quenched. In this case, intrinsic anisotropy is found to be $-0.02 < \Delta < 0.02$, and Cu pyrazine compounds have $\Delta \leqslant 0.01$ in general [13,15,16].

One may also note that the interlayer coupling term with J' in Eq. (1) would become less relevant compared to the Zeeman term with strong H. It is estimated that $J'/J = 4.4 \times 10^{-2}$ from the empirical formula $J'/J = \exp(2.43 - 4\pi \times 0.183J/k_BT_N)$ [4]. This gives us $J'/k_B = 0.42\,\mathrm{K}$, which is outweighed by the Zeeman energy $g\mu_B\mu_0 H/k_B = 9.4\,\mathrm{K}$ for 7 T that is similar to J/k_B.

Figure 4 shows the susceptibility $\chi = M/H$, where M is magnetization, as a function of temperature for various magnetic fields. Arrows indicate T_N obtained from the NMR in this work [28] and the previous zero-field powder neutron diffraction [27] where T_N is assumed not to change appreciably from 0 to 50 mT. No clear feature for the transition is observed in $\chi(T)$ across T_N. The broad maxima observed near 8 K, for both $H \parallel c$ and $H \parallel ab$, are known to be characteristic of low-dimensional and/or frustrated antiferromagnets where T_N is suppressed by fluctuation. For $H \parallel c$, χ shows a minimum as a function of temperature for a field up to 2 T, where the temperature with minimum χ is nearly H independent. This minimum feature gradually disappears with further increasing H, and is not visible at 7 T. For $H \parallel ab$, by contrast, χ monotonically decreases with decreasing temperature at very low fields up to 10 mT. The χ minimum as a function of temperature appears in a field above 20 mT, and the temperature with minimum χ increases with increasing H up to 2 T. This minimum feature again disappears with further increase of the field much like the $H \parallel c$ case. In the following, we first discuss the observation based on impurities, and then a possibility of spin-anisotropy crossover.

The χ minimum for $H \parallel c$ could be due to a few percent of paramagnetic impurities that give rise to a Curie tail at

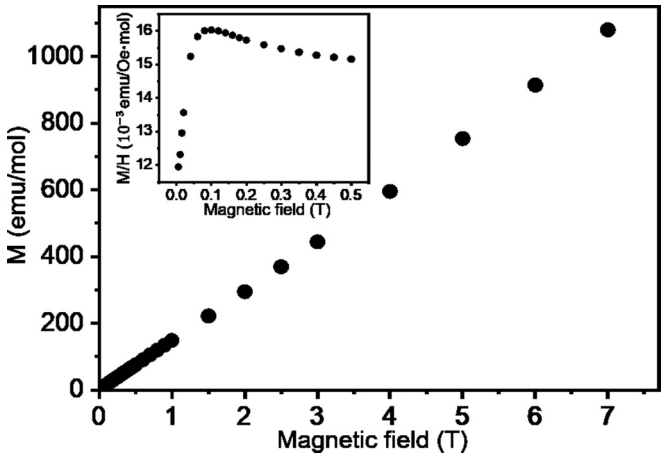

FIG. 5. Isothermal magnetization M as a function of H for $H \parallel ab$ at 1.8 K. Inset plots M/H as a function of H.

low temperatures [27]. The Curie tail and the resulting χ minimum could be gradually masked by the increasing χ with H in high fields that was hinted by the previous $M(H)$ measurements on a powder [27]. For $H \parallel ab$, the impurity contribution at low fields would be much less apparent due to the strongly decreasing χ with decreasing temperature. In any case, however, no paramagnetic impurity contribution is evident in our $M(H)$ data shown in Fig. 5.

It is interesting to look into the results with the spin-anisotropy crossover scenario [9,10,18]. Indeed the χ curves in Fig. 4 look quite similar to those previously reported in other square-lattice antiferromagnets, including $Sr_2CuO_2Cl_2$ [17] and Cu pyrazine compounds [13,16], where the χ minimum was attributed to the spin-anisotropy crossover. In these experiments, the χ minimum or crossover temperature T_{CO} was observed only slightly above T_N, in contrast to the present work (see Fig. 4). The QMC simulation predicts $T_{CO} > T_N$ for the pure 2D cases, that is, J' being set to zero [10,18]. As a possibility, the crossover might be still observed just below T_N where there remain strong spin fluctuations. In case the crossover scenario applies, the χ minimum for $H \parallel ab$ at low fields could indicate the crossover from the intrinsic XY to the field-induced Ising anisotropy. For instance, at 30 mT, the field-induced anisotropy is expected as $\Delta_H \sim 7.7 \times 10^{-6}$, which for $Sr_2CuO_2Cl_2$ corresponds to the applied field of 4.7 T where the crossover was indeed observed [12].

The isothermal magnetization $M(H)$ for $H \parallel ab$ at 1.8 K, as shown in Fig. 5, seemingly increases linearly with H. However, a slight variation in the slope of $M(H)$ can be seen when M/H is plotted against H as shown in the inset. The ratio of an anisotropy field [where a kink or slope change occurs in $M(H)$] to the saturation field could be used to estimate the anisotropy Δ [13,15]. We tentatively take the value of 0.1 T, where the M/H against H shows a maximum (see the inset), as the anisotropy field. This gives an estimate of $\Delta = 4 \times 10^{-3}$ with the expected saturation field of 25 T [27], which is of the same order of magnitude as those of many known Cu-pyz square lattice antiferromagnets [6,13,15].

Lastly, we comment on the role of interlayer coupling. For pure 2D Heisenberg antiferromagnets with the XY anisotropy of 0.004, the Berezinskii-Kosterlitz-Thouless (BKT) transition is expected at $T_{BKT} = 0.196J/k_B$ [18], which becomes about 1.8 K for $[CuCl(pyz)_2]BF_4$. The observed T_N is higher than twice T_{BKT}, which reflects the effects of the interlayer coupling. Considering the combined effects of J' and Δ on T_c, especially when they are comparable to each other, must be a challenge. The estimated $J'/J \sim 4.4 \times 10^{-2}$ builds on the Heisenberg model [4], and provides an upper limit in the presence of anisotropy Δ. Keeping the latter caution in mind, it is still interesting to note a possibility of realizing $J'/J > \Delta$. By contrast, for most other known $[Cu(pyz)_2]^{2+}$ compounds [6,13,15], the estimation gives $J'/J \lesssim \Delta$ as $10^{-4} \lesssim J'/J \lesssim 10^{-2}$ and $10^{-3} \lesssim \Delta \lesssim 10^{-2}$. Similarly, $J'/J < \Delta$ for $Sr_2CuO_2Cl_2$ as $J'/J \sim 10^{-4}$ and $\Delta \sim 10^{-3}$. The relatively large J'/J with respect to Δ may support the above anisotropy crossover scenario: Since T_N would increase with increasing J' while T_{CO} would be lower for smaller Δ, the crossover in $[CuCl(pyz)_2]BF_4$, if any, is expected at relatively low temperature compared to $Sr_2CuO_2Cl_2$ or other $[Cu(pyz)_2]^{2+}$ compounds, which is consistent with our data.

IV. CONCLUSION

The critical properties of the quasi-2D Heisenberg antiferromagnet $[CuCl(pyz)_2]BF_4$ vary depending on the applied magnetic field. On increasing the magnetic field strength, the 3D ordering transition temperature T_N increases while the order-parameter exponent β decreases. These are likely due to enhanced spin anisotropy by the interplay of the applied field and the intralayer exchange interaction. The relatively large $\beta \simeq 0.29$ in low field implies the importance of the interlayer coupling. Magnetic susceptibility as a function of temperature shows a minimum below T_N in low fields which disappears in high fields. Some paramagnetic impurities could be responsible for this, while a possibility of a spin-anisotropy crossover is also discussed in light of the relatively strong interlayer coupling.

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