Magnetic properties of the quasi-two-dimensional $S = \frac{1}{2}$ Heisenberg antiferromagnet $[\text{Cu(pyz)}_2(\text{HF}_2)]\text{PF}_6$

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We report on high-field magnetization, specific-heat and electron spin resonance (ESR) studies of the quasi-two-dimensional spin-1/2 Heisenberg antiferromagnet $[\text{Cu(pyz)}_2(\text{HF}_2)]\text{PF}_6$. The frequency-field diagram of ESR modes below $T_N = 4.38$ K is described in the frame of the mean-field theory, confirming a collinear magnetic structure with an easy-plane anisotropy. The obtained results allowed us to determine the anisotropy/exchange interaction ratio, $A/J = 0.003$, and the upper limit for the inter/intra-plane exchange-interaction ratio, $J'/J = 1/16$. It is argued that despite the onset of 3D long-range magnetic ordering the magnetic properties of this material (including high-magnetic-field magnetization and non-monotonic field dependence of the Néel temperature) are strongly affected by two-dimensional spin correlations.

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I. INTRODUCTION

Recently, a considerable amount of attention has been devoted to the theoretical and experimental investigation of two-dimensional (2D) quantum spin systems. In case of the ideal 2D Heisenberg antiferromagnet (AF) on a square lattice, the magnetic long-range order is suppressed by zero-point fluctuations at any finite temperature. However, the presence of an easy-axis anisotropy can induce a finite-temperature phase transition into the Néel ordered state. On the other hand, for an easy-plane anisotropy, a transition of the Berezinskii-Kosterlitz-Thouless (BKT) type was proposed, where the high-temperature disordered phase can be described as a gas of vortices. Below the BKT transition ($T_{BKT}$), the vortices are bound in vortex-antivortex pairs, and the spin-spin correlation decay changes from exponential to algebraic. A crossover from the isotropic to XY behavior in low fields has been predicted for 2D Heisenberg AF.

Interplane interactions (which are always present in real materials) can significantly modify the ground-state properties of quasi-2D systems, inducing for instance a phase transition with three-dimensional (3D) long-range magnetic order. Due to the onset of 3D ordering in most real materials, the critical behavior of diverging quantities as anticipated for ideal 2D systems at $T_{BKT}$ is hardly observable experimentally.

The quasi-2D Heisenberg AF model with interplane interactions can be described by the Hamiltonian

$$\mathcal{H} = J \sum_{<i,j>_a} \mathbf{S}_i \cdot \mathbf{S}_j + J' \sum_{<i,j>_c} \mathbf{S}_i \cdot \mathbf{S}_j - \beta \sum_i S^z_i, \quad (1)$$

with $\beta = g \mu_B B$, where $\mu_B$ is the Bohr magneton, $J$ and $J'$ are the intra- and interplane exchange interactions, respectively, and $<i,j>_a$ and $<i,j>_c$ correspond to nearest-neighbor spin pairs formed in the directions parallel and perpendicular to the $S = 1/2$ planes, respectively. The variation of the ratio $J'/J$ allows to study nicely the rich phase diagram of quasi-2D magnetic systems, including the transition from a 2D Heisenberg AF ($J'/J = 0$) to the 3D Heisenberg AF ($J'/J = 1$). Remarkably, even in presence of relatively strong interplane interactions, the 2D quantum fluctuations can significantly affect the magnetic properties of such systems, resulting, for instance, in a peculiar non-monotonic field dependence of the ordering temperature. Such a behavior has recently been observed in the quasi-2D square-lattice Heisenberg AF $[\text{Cu(C}_4\text{H}_8\text{N}_2)_2(\text{HF}_2)]\text{BF}_4$ and in the spatially anisotropic triangular magnet $\text{Cu(tn)}\text{Cl}_2$ where tn is 1,3-diaminopropane ($\text{C}_3\text{H}_{10}\text{N}_2$).

Here, we report on magnetic properties of single-crystalline samples of $[\text{Cu(pyz)}_2(\text{HF}_2)]\text{PF}_6$, which is regarded as a nearly perfect realization of a quasi-2D $S = 1/2$ Heisenberg AF. Comprehensive specific-heat, high-field magnetization and electron spin resonance (ESR) studies allow us to identify a long-range ordered Néel state with easy-plane anisotropy and to accurately estimate the spin-Hamiltonian parameters. We show that in spite of the onset of the 3D ordered state below $T_N$, the magnetic properties of $[\text{Cu(pyz)}_2(\text{HF}_2)]\text{PF}_6$ are still significantly affected by 2D spin correlations.

II. EXPERIMENTAL DETAILS

The measurements have been performed at the Dresden High Magnetic Field Laboratory (Hochfeld-Magnetlabor Dresden, HLD). The pulsed-field magnetization was obtained by integrating the voltage induced in a compensated pick-up coil system containing a sample. The low-field magnetization below 7 T was mea-
will be removed from the current database.

It is a good practice to always have a backup of the data before removing it from the database.
FIG. 3: (Color online) (a) Temperature dependence of the specific heat of \([\text{Cu(pyz)}_2(\text{HF}_2)]\text{PF}_6\) for \(B \parallel \text{ab}\) (blue symbols) and \(B \parallel c\) (red symbols). The experimental data are shifted by 1 J mol\(^{-1}\) K\(^{-1}\) per Tesla. (b) The \(B - T\) phase diagram of \([\text{Cu(pyz)}_2(\text{HF}_2)]\text{PF}_6\) obtained from the specific-heat data (full symbols) shown together with the calculated phase diagram for the ideal 2D case with \(J' = 0\) (open symbols). Lines are guides to the eye.

Using the exchange coupling, obtained from the high-field magnetization data, and \(T_N = 4.38\) K we find \(J'/J = 0.014\), which is in excellent agreement with our previous estimate.

ESR is a powerful technique to determine the magnetic structure and the effective spin-Hamiltonian parameters of in exchange-coupled spin systems. At room temperature, a single ESR line was observed for all field orientations with a typical sinusoidal angular dependence of the \(g\)-factor expected for a Cu\(^{2+}\) ion in an octahedral surrounding with an axial symmetry due to the Jahn–Teller effect. The results confirm that the main exchange paths between the magnetic ions are formed in the \(ab\) planes by \(d_{x^2-y^2}\) orbitals, which directly overlap with orbitals of pyrazine ligands, creating a quasi-2D network of exchange coupled Cu\(^{2+}\) ions.

The temperature evolution of the ESR spectra in \([\text{Cu(pyz)}_2(\text{HF}_2)]\text{PF}_6\) measured at 90 GHz for \(B \parallel c\) is shown in Fig. 4. The temperature dependence of the resonance field, the linewidth, and the integrated intensity of the ESR lines in fields applied parallel and perpendicular to the \(ab\) plane are shown in Fig. 5(a)-(b) and Fig. 6. It is evident that in the vicinity of the ordering temperature \((T_N \approx 4.6\) K at 3 T), a region of enhanced short-range spin correlations is entered and both the resonance field and the linewidth change dramatically. It is important to mention that the integrated ESR intensity is proportional to the dynamic spin susceptibility. In Fig. 6 the temperature dependence of \(M/B\) (measured using a SQUID magnetometer with applied magnetic field \(B = 3\) T), the integrated ESR intensity, and the magnetic susceptibility calculated for a 2D Heisenberg AF system are presented. The results of the calculations are in good agreement with our experimental data above \(T_N\) for \(J/k_B = 12.8\) K, proving the crucial role of 2D spin correlations in \([\text{Cu(pyz)}_2(\text{HF}_2)]\text{PF}_6\).

The frequency-field diagram of the ESR signals is presented in Fig. 7. Well above the critical temperature \((T = 15\) K), we observe only one resonance mode for each orientation, \(B \parallel c\) and \(B \parallel ab\), as shown in the inset of Fig. 7. The frequency-field dependence of the these modes corresponds to transitions between the energy levels of the \(S = 1/2\) Cu\(^{2+}\) ions and can be described by \(\hbar \nu = g_\parallel \mu_B B\) with \(g_\parallel = 2.28\) and \(g_{ab} = 2.05\).

The ESR excitation spectrum changes dramatically below \(T_N\), as shown for \(T = 1.3\) K in Fig. 7. Two modes, \(\omega_1\) and \(\omega_2\), are observed when the magnetic field is applied in the \(ab\) plane. For \(B \parallel c\), a nonlinear dependence of the mode \(\omega_4\) was observed. Most importantly, in the ESR excitation spectrum the AF resonance gap was determined by us directly, \(\Delta = 43\) GHz \((\approx 2\) K) at \(B = 0\). Such a frequency-field diagram is a textbook example for magnetic excitations in a system with collinear 3D AF long-range order and easy-plane anisotropy. The
FIG. 5: (Color online) Temperature dependence of the resonance field (a) and linewidth (b) obtained from ESR data measured at $\nu = 90$ GHz for a magnetic field aligned parallel (empty squares) and perpendicular (empty circles) to the $ab$ plane. The transition temperature, $T_N = 4.64$ K, as obtained from specific-heat measurements at 3 T for $B || ab$ (Fig. 3) is shown by the dotted line.

The frequency-field dependence of the antiferromagnetic resonance modes can be calculated using the mean-field approximation:

$$\omega_1/\gamma = B,$$

$$\omega_2/\gamma = \sqrt{2B_AB_E - (B_A/2B_E)B^2},$$

for magnetic fields applied parallel to the easy plane and

$$\omega_3/\gamma = 0,$$

$$\omega_4/\gamma = \sqrt{2B_AB_E + (1 - B_A/2B_E)B^2},$$

for magnetic fields applied perpendicular to the easy plane, where $\gamma = g\mu_B/\hbar$ is the gyromagnetic ratio, $B_E$ and $B_A$ are the exchange and anisotropy field, respectively. Our results clearly show that below $T_N$ the $ab$ plane is the easy plane, along which the magnetic moments are aligned at $B = 0$. The frequency-field diagram was analyzed using the Eqs. 3 – 6. The best fit was obtained for $B_E = 18.72$ T and $B_A = 0.05$ T. The exchange field, $B_E$, is related to the exchange coupling by the simple relation $B_E = 4SJ/\hbar\gamma$ and yields $J/k_B = 12.9$ K, which is in perfect agreement with the value of the intra-plane exchange coupling obtained from our magnetization and specific-heat measurements. Noticeably, using ESR data, the anisotropy constant ($\sim 0.3\%$ of the exchange interaction) can be estimated, revealing the validity of isotropic quasi-2D $S=1/2$ Heisenberg model applied to $[\text{Cu(pyz)}_2(\text{HF}_2)]PF_6$.

FIG. 6: (Color online) Temperature dependence of $M/B$ measured at $B = 3$ T (open symbols) and the integrated intensity obtained from ESR data measured at $\nu = 90$ GHz (full symbols). The data are presented together with the calculated results (solid line) for a 2D square-lattice Heisenberg AF system with $J/k_B = 12.8$ K.

IV. CONCLUSION

Our comprehensive specific-heat, high-field magnetization, and ESR studies revealed the important role of 2D spin correlations on the magnetic properties of the $S = 1/2$ quasi-2D Heisenberg AF $[\text{Cu(pyz)}_2(\text{HF}_2)]PF_6$. The observation of two AF resonance modes below $T_N$ confirms the presence of a 3D collinear AF long-range ordered state with an energy gap of $\Delta = 43$ GHz in the magnetic excitation spectrum and $A/J \sim 0.003$ for $T = 1.3$ K, AFMR.
the anisotropy/exchange interaction ratio. The presence of a field-induced XY behavior has unambiguously been identified by the observation of a peculiar non-monotonic field dependence of the ordering temperature.

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