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High-field magnetization study of the $S=\frac{1}{2}$ antiferromagnetic Heisenberg chain $[PM\,Cu(NO_3)_2(H_2O)_2]_n$ with a field-induced gap

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We present a high-field magnetization study of the $S=\frac{1}{2}$ antiferromagnetic Heisenberg chain $[PM\,Cu(NO_3)_2(H_2O)_2]_n$. For this material, as result of the Dzyaloshinskii-Moriya interaction and a staggered g tensor, the ground state is characterized by an anisotropic field-induced spin excitation gap and a staggered magnetization. Our data reveal the qualitatively different behavior in the directions of maximum and zero spin excitation gap. The data are analyzed via exact diagonalization of a linear spin chain with up to 20 sites and on basis of the Bethe ansatz equations, respectively. For both directions we find very good agreement between experimental data and theoretical calculations. We extract the magnetic coupling strength J/k_B along the chain direction to 36.3(5) K and determine the field dependence of the staggered magnetization component m_s.

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Motivated by the rich variety of different magnetic ground states, such as quantum critical behavior or gaps in the spin excitation spectra, quasi-one-dimensional quantum magnets have been the focus of intense experimental and theoretical research efforts in recent years.[1–4] To gain deeper insight into the physics of such quantum spin systems well-defined model compounds need to be explored. Here, the uniform $S=\frac{1}{2}$ antiferromagnetic Heisenberg chain (AFHC) is of particular interest, since it is exactly solvable using the so-called Bethe ansatz equations.[5–7]

In $S=\frac{1}{2}$ AFHC's, lacking inversion symmetry, additional terms in the Hamiltonian have to be taken into account, that is the Dzyaloshinskii-Moriya (DM) interaction and an alternating g tensor.[8,9] This gives rise to an effective staggered field h_s perpendicular to the applied magnetic field H. Then the Hamiltonian is written as[8,9]

$$\hat{H}=J\sum_i\,[\mathbf{S}_i\mathbf{S}_{i+1}-h_u S_i^z-(-1)^i h_s S_i^x] \qquad (1)$$

with J as the coupling constant, $h_u=g\mu_B H/J$ as the effective uniform field, and h_s as the induced effective staggered field. In the following we refer to this as the *staggered* $S=\frac{1}{2}$ AFHC model. Resulting from this extension of the uniform $S=\frac{1}{2}$ AFHC are the opening of an anisotropic spin excitation gap with application of a magnetic field and new, particlelike excitations such as solitons, antisolitons, and their bound state, the ''breather.''[10,11] Moreover, by fully evaluating the effect of the DM interaction on the ground-state properties, a crossover to a qualitatively different high-field behavior has been predicted recently.[12]

The model for the staggered $S=\frac{1}{2}$ AFHC has been used to describe two materials in particular, copper benzoate[3] and copper pyrimidine nitrate $[PM\,Cu(NO_3)_2(H_2O)_2]_n$.[13] For the latter compound, from a single-crystal study a magnetic exchange parameter $J/k_B=36$ K is derived. Further, an additional Curie-like contribution to the magnetic susceptibility at low temperatures is observed, which varies strongly with magnitude and direction of the applied external field. Specific-heat measurements in magnetic fields verify the predicted formation of an anisotropic spin excitation gap, whose magnitude also depends on size and orientation of the external field.[13] The spin excitation gap and the Curie-like contribution to χ are largest for the same field direction (referred to as c'', for notation see Ref. 13) and vanish for one direction perpendicular to c'' in the a-c plane (referred to as a'').

For $S=\frac{1}{2}$ AFHC materials, (high-field) magnetization experiments are abundant and are perfectly described by theory.[1,14–18] Recently, for the staggered $S=\frac{1}{2}$ AFHC the magnetization curve has been calculated by several groups.[12,19–21] As yet, these theoretical predictions have not been verified experimentally.

Therefore, in this Rapid Communication we present a magnetization study on $[PM\,Cu(NO_3)_2(H_2O)_2]_n$ covering the entire field range up to saturation, i.e., $\mu_0 H=53$ T. With our study of the magnetization along a'' and c'' we establish the contrasting behavior along these two directions, the first representing the uniform, and the latter the staggered $S=\frac{1}{2}$ AFHC. The behavior of the uniform $S=\frac{1}{2}$ AFHC is evaluated on basis of the Bethe ansatz equations.[7,18] In contrast, for the staggered $S=\frac{1}{2}$ AFHC we analyze our data by means of exact diagonalization of linear chains with up to $N=20$ spins, based upon the staggered field theory by Oshikawa and Affleck.[8,9] From this analysis we find very good agreement between experimental data and theoretical calculations. We determine the characteristic parameters, i.e., the coupling constant J/k_B and the staggered magnetization m_s.

Comparing our finite-size calculations to previous density-matrix renormalization group (DMRG)

studies[12,19–21] for the Hamiltonian (1), we find perfect agreement between our results and those of other groups. Only for low-fields finite-size effects are present. The advantage of our finite-size calculations compared to the DMRG method lies in its simplicity and short computation time.

Single crystals of $[\mathrm{PM\,Cu(NO_3)_2(H_2O)_2}]_n$ have been grown by slow evaporation of the equimolar aqueous solution of copper nitrate and pyrimidine.[22] The crystals show well-defined facets and the principal axes can be identified easily. We have checked by low-field magnetization measurements that the magnetic susceptibility matches the one published in Ref. 13. For the magnetization measurements the samples were oriented along the characteristic orientations a'' and c'' (misalignment $\leqslant 5°$), glued to the tip of a plexi glass rod and placed inside a thin walled teflon cylinder. The magnetization signal of the sample holder was negligible.

Magnetization measurements were carried out at the Laboratoire National des Champs Magnétiques Pulsés in Toulouse in pulsed magnetic fields up to $\mu_0 H = 53$ T. Pulsed magnetic fields were obtained by discharging a capacitor bank in a solenoid according to a crowbar described in Ref. 23. The pulse duration was about 200 ms with an increasing time of 25 ms. The magnetization was detected as a voltage V induced in a compensated arrangement of pick-up coils wound concentrically around the sample and coupled to it with the coupling constant η, such that $V = \eta\Omega\,\delta M/\delta t$, with Ω as the sample volume.[24] The absolute magnetization was obtained by numerical integration of this voltage. Due to the limited sample space (diameter <1.6 mm), the absolute signal was small ($<10^{-5}$ Am^2). To achieve a higher accuracy of the signal calibration additional measurements were performed in magnetic fields up to 5 T in a commercial superconducting quantum interference device magnetometer.

In Fig. 1 we present the magnetization curve of $[\mathrm{PMCu(NO_3)_2(H_2O)_2}]_n$ as a function of field at 1.6 and 4.2 K for the two characteristic orientations, i.e., $H||a''$ [Fig. 1(a)] and $||c''$ [Fig. 1(b)], respectively. Comparing the magnetization along the two directions, an anisotropic response is observed. At 1.6 K for $H||a''$ we find the archetypical behavior of the $S=\frac{1}{2}$ AFHC.[17] In contrast, for fields parallel to the c'' axis an additional low-field contribution and a delayed saturation of the magnetization occurs. To emphasize this difference in the insets of Figs. 1(a) and 1(b) we plot the derivatives of the magnetization, $dM/d(\mu_0 H)$. For small fields $||c''$ the initial slope is more than twice as large as for the a'' axis. At high fields (>35 T) the saturation of the magnetization for $H||c''$ is suppressed, as indicated by a smaller, broader feature in $dM/d(\mu_0 H)$, as compared to the a'' axis response. Increasing the temperature to 4.2 K reduces the difference in the $M(\mu_0 H)$ curves between the two directions, but does not completely suppress it.

The deviation from the uniform $S=\frac{1}{2}$ AFHC behavior along the c'' direction is attributed to an additional magnetization component. It increases much faster and passes through a maximum at a much lower field than the uniform saturation field $\mu_0 H_{sat}$. Since the second component is not present along a'', we ascribe it to the staggered magnetization m_s.

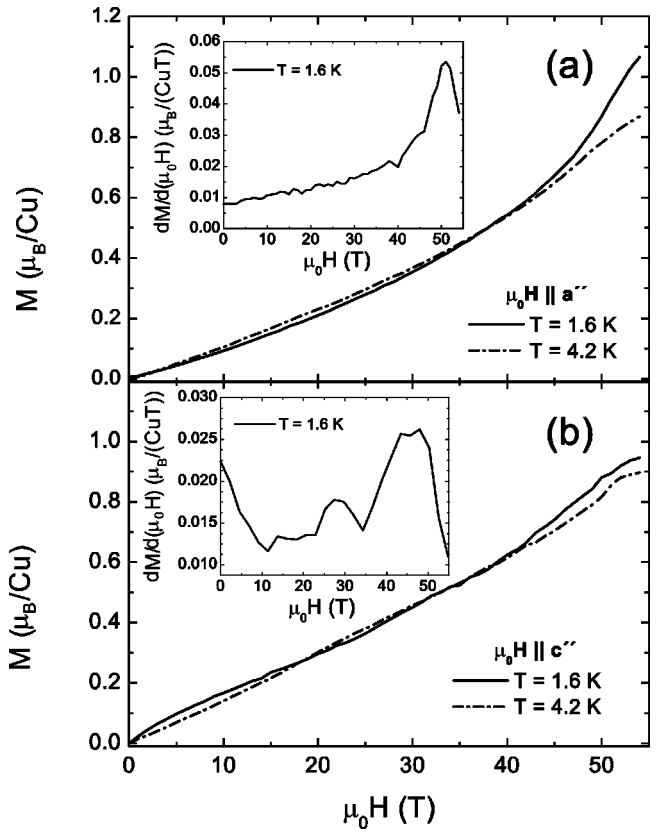

FIG. 1. The field dependence of the magnetization of $[\mathrm{PM\,Cu(NO_3)_2(H_2O)_2}]_n$ with the external field aligned along the a'' (a) and the c'' direction (b). In the insets, the field derivative $dM/d(\mu_0 H)$ is displayed.

The g tensor of $[\mathrm{PM\,Cu(NO_3)_2(H_2O)_2}]_n$ has been derived from electron spin resonance measurements.[13] In the uniform $S=\frac{1}{2}$ AFHC model the saturation field is calculated according to the formula[9]

$$H_c = 4JS/g\mu_B. \tag{2}$$

For zero temperature and by using $J/k_B = 36 \pm 0.5$ K, $g_{a''} = 2.14 \pm 0.02$, and $g_{c''} = 2.21 \pm 0.02$ from Ref. 13, we obtain $\mu_0 H_{sat} = 50.1 \pm 0.8$ T and 48.5 ± 0.8 T along a'' and c'' axes, respectively. The saturation magnetization M_s is calculated to $M_{s,a''} = 1.07 \pm 0.01\ \mu_B$/Cu atom and $M_{s,c''} = 1.11 \pm 0.01\ \mu_B$/Cu atom. Thus, for the uniform $S=\frac{1}{2}$ AFHC at $T = 1.6\ \mathrm{K} \ll J/k_B$, the saturation magnetization should be approached at highest experimental applied field. Indeed for $H||a''$ [Fig. 1(a)], the $T=1.6$ K curve has an initial slope lower than at 4.2 K. With increasing field the curvature becomes larger, crosses the 4.2 K curve near 38 T and almost reaches saturation at ≈ 53 T. The data for both temperatures become nonlinear with field for $\mu_0 H > 15$ T. Moreover, with decreasing temperature the data sets approach the $T=0$ curve for the uniform $S=\frac{1}{2}$ AFHC in full agreement with previous experimental work.[17]

From a theoretical point of view, the magnetization curve of the uniform $S=1/2$ AFHC has been computed for $T=0$ by Bethe ansatz.[14] However, our measurements have been carried out at temperatures $T > 0.04J$, where thermal fluctua-

tions lead to a substantial rounding of the cusp at the saturation field in the $T=0$ magnetization curve. On the other hand, at 1.6 K we have $T<0.05J$, substantially smaller than the lowest corresponding temperature studied in Ref. 17 for copper pyrazine dinitrate. Even at $T=0.05J$, the magnetization curve computed for the uniform $S=\frac{1}{2}$ AFHC on a ring with $N=16$ sites still exhibits clear finite-size effects, precluding an analysis along the lines of Ref. 17. We therefore use results obtained by the thermodynamic Bethe ansatz in the thermodynamic limit $N=\infty$ and at arbitrary temperature T to describe the magnetization curve for $H\|a''$.[18]

The situation for $H\|c''$ is quite different. On one hand, the Hamiltonian (1) cannot be solved exactly with a nonzero staggered field h_s and we therefore have to rely on a numerical treatment. Whereas the z component S^z of the total spin is conserved for $h_s=0$, even this is not the case anymore for $h_s\neq 0$. This has two consequences: (i) The reduced symmetry of the Hamiltonian (1) restricts the system sizes N that can be accessed, and (ii) each new set of magnetic fields h_u and h_s requires a new numerical determination of the ground state. On the other hand, the field-induced opening of a gap[8,9] leads to the following two simplifications: (i) For the high magnetic fields studied here, the gap is sufficiently large to suppress thermal excitation at low temperatures. Therefore, finite temperature is expected to have only a comparatively small effect. Indeed, this is confirmed by the difference of the $T=1.6$ and 4.2 K curves in Fig. 1, which are noticeably smaller along the c'' direction [panel (b)] than for the a'' one [panel (a)]. This permits us to compare a measurement at low but finite temperature with a computation at $T=0$. (ii) In most field ranges considered here, the correlation length turns out to be sufficiently short such that finite-size effects can be neglected already for systems with only $N=20$ sites. More precisely, the correlation length is large only for a small staggered field h_s and thus only the low-field region suffers from finite-size effects. These lead to an artificial low-field peak in the staggered magnetization m_s [see e.g., dashed curve in Fig. 2(b)] whose position roughly determines the region up to which finite-size effects are still relevant, as evidenced by comparison with results for $N\leqslant 16$ (not shown). Due to the fast disappearance of finite-size effects for higher magnetic fields it is completely sufficient for our purposes to apply the Lanczos diagonalization procedure to rings with $N\leqslant 20$ sites. Therefore, the additional effort of a DMRG procedure[12,19–21] is not necessary here.

A final remark is in order before we present our numerical results and compare them with the experiment. In the presence of a staggered field $h_s=ch_u$, which is related by a constant anisotropy parameter c to the uniform field h_u, the physical magnetization m_{phys} (which is measured experimentally) is given by the superposition of the uniform m_u and staggered m_s magnetization components:[8,9]

$$m_{phys}=m_u+cm_s. \tag{3}$$

To our knowledge, previous numerical works[12,19–21] only showed m_u and m_s separately, while numerical results for the combination m_{phys} [Eq. (3)] have not been published yet.

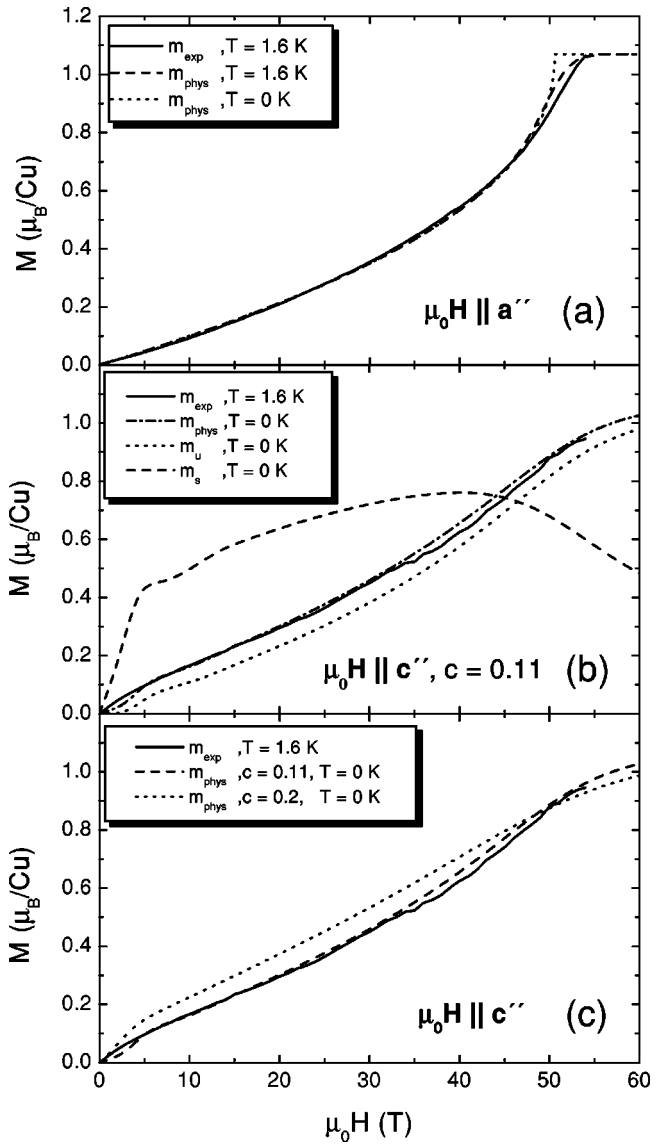

FIG. 2. Experimental and theoretical magnetization curves for $[PM\,Cu(NO_3)_2(H_2O)_2]_n$ at $T=1.6$ K for different field directions. (a) $\mu_0 H||a''$: solid line—experimental data, dashed line—fit assuming uniform $S=\frac{1}{2}$ AFHC for $T=1.6$ K, dotted line—$T=0$ calculations.[18] (b) $\mu_0 H||c''$: dotted line—uniform magnetization m_u, dashed line—staggered magnetization m_s, dash-dotted line—calculated physical magnetization m_{phys} for $c=0.11$, solid line—experimental data. (c) $\mu_0 H||c''$: dashed line—m_{phys} for $c=0.11$, dotted line—m_{phys} for $c=0.2$, solid line—experimental data.

For the magnetization along a'' [Fig. 2(a)], using $\mu_0 H_{sat}=50.6$ T, $g_{a''}=2.14$, and taking into account the finite experimental temperature, we find very good agreement between our data and the Bethe ansatz result.[18] The deviations for fields $\mu_0 H>50$ T can be attributed to the misalignment of the crystal, while for smaller fields experimental data and calculated result match within 2%. Thus, for this field direction the uniform $S=\frac{1}{2}$ AFHC is established.

In Fig. 2(b) we depict the field dependence of the magnetization along c''. For fields $\mu_0 H>10$ T we can fully describe these data on basis of the staggered $S=\frac{1}{2}$ AFHC

model using $\mu_0 H_{sat} = 49.3$ T, $g_{c''} = 2.19$. Here, we have used an anisotropy parameter $c = 0.11$. This value has been obtained from a comparison of the data and calculations for $c \in [0.08;0.12]$, step size 0.01, as the optimum solution. The values $\mu_0 H$ along a'' and c'' are fully consistent with those predicted from Eq. (2) within their error bars. On average, the saturation fields $\| c''$ and $\| a''$ correspond to a magnetic coupling strength $J/k_B = 36.3(5)$ K.

With the value of the anisotropy parameter c we can decompose m_{phys} into the uniform (m_u) and staggered (m_s) component, according to Eq. (3). Both, m_u and m_s, are included in Fig. 2(b). Their field dependence closely resembles the ones obtained in Ref. 20 for the case $h_u = 10 h_s$. Specifically, we find that m_s traverses a maximum at ~ 40 T, while m_u and m_s approach finite but nonsaturated values for largest fields. Our analysis establishes the staggered $S = \frac{1}{2}$ AFHC for the c'' axis of $[\mathrm{PM\,Cu(NO_3)_2(H_2O)_2}]_n$.

Further, we performed calculations for c values in the range 0.08–0.28. The cases $c = 0.2$ and 0.11 are depicted in Fig. 2(c). From these data it appears that for decreasing parameter c the curvature of m_{phys} increases and approaches the uniform $S = \frac{1}{2}$ AFHC magnetization behavior for vanishing staggered field h_s, as expected. With the definition of the Hamiltonian of the staggered $S = \frac{1}{2}$ AFHC model in Ref. 13 the anisotropy parameter $c = 0.11$ from this work translates into a value 0.24.[25] Thus, we find perfect agreement of our c value with the one obtained from magnetic susceptibility measurements in Ref. 13, i.e., $c = 0.235$.

In conclusion, we have performed high-field magnetization experiments on $[\mathrm{PM\,Cu(NO_3)_2(H_2O)_2}]_n$ at temperatures 1.6 and 4.2 K. We analyzed our data by means of Bethe ansatz equations for the experiments along the a'' axis and exact diagonalization of linear chains containing $N = 20$ spins, based upon the staggered field theory by Oshikawa and Affleck,[8,9] for the c'' axis. The very good agreement of our data with our theoretical calculations and those of other groups[19,20] verifies the predictions for the uniform and staggered $S = \frac{1}{2}$ AFHC models. This way, for the staggered case we have extracted the staggered magnetization component $m_s(\mu_0 H)$.

Recently, for the staggered $S = \frac{1}{2}$ AFHC model a low-field/high-field crossover in the staggered magnetization has been predicted.[12] For $[\mathrm{PM\,Cu(NO_3)_2(H_2O)_2}]_n$ these calculations would imply deviations from the staggered behavior in the field range $\mu_0 H > 50$ T, and thus cannot be observed in our study. To verify the predictions from Ref. 12, in the future it will be interesting to perform analogous magnetization studies on related materials with smaller J values.

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[24] Measurements were made for increasing and decreasing field. No hysteresis has been observed. For clarity, because of a higher signal-to-noise ratio, in the figures we only present data taken for decreasing field.
[25] Due to different prefactors in the Hamiltonian from Ref. 13 and in Eq. (1) of this work the g factor has to be multiplied with our c value to obtain the anisotropy parameter from Ref. 13.