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Field-Induced Gap in a Quantum Spin-1/2 Chain in a Strong Magnetic Field

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Magnetic excitations in copper pyrimidine dinitrate, a spin-1/2 antiferromagnetic chain with alternating g-tensor and Dzyaloshinskii-Moriya interactions that exhibits a field-induced spin gap, are probed by means of pulsed-field electron spin resonance spectroscopy. In particular, we report on a minimum of the gap in the vicinity of the saturation field $H_{sat} = 48.5$ T associated with a transition from the sine-Gordon region (with soliton-breather elementary excitations) to a spin-polarized state (with magnon excitations). This interpretation is fully confirmed by the quantitative agreement over the entire field range of the experimental data with the DMRG calculations for spin-1/2 Heisenberg chain with a staggered transverse field.

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Introduction.— Due to recent progress in theory and the growing number of physical realizations, low-dimensional quantum magnets continue to receive a considerable amount of attention. They serve as model systems for investigating numerous fascinating phenomena in materials with cooperative ground states, in particular, induced by high magnetic fields. The way a magnetic field changes the ground-state properties and, correspondingly, the low-energy excitation spectrum of low-dimensional magnets is one of the fundamental aspects in quantum magnetism. For example, the zero-field ground state of an isotropic $S = 1/2$ Heisenberg antiferromagnetic (AF) chain with uniform nearest-neighbor exchange coupling is a spin singlet, and its spin dynamics is determined by a gapless two-particle continuum of fractional $S = 1/2$ excitations, called spinons. Application of an external magnetic field H leads to a pronounced rearrangement of the excitation spectrum, making the soft modes incommensurate [1, 2] but leaving the spinon continuum gapless. However, in a fully spin-polarized phase, $H > H_{sat}$, the excitation spectrum is gapped and dominated by ordinary spin waves (magnons). The low-energy excitation spectrum of such an ideal isotropic Heisenberg $S = 1/2$ chain can be described in terms of an effective free massless boson theory [3–5].

The presence of additional interactions such as Dzyaloshinskii-Moriya (DM) interaction[7] can significantly alter the physical properties of such spin systems (see for instance Ref. [6]), and, in particular, their high-field behavior. A Heisenberg spin-1/2 chain with exchange interaction J and DM interaction (or alternating g-tensor) in a field H can be mapped to a simple Heisenberg chain with a staggered transverse field $h \propto H$ [8–10], described by the effective spin Hamiltonian

$$\mathcal{H} = \sum_j \left[J\mathbf{S}_j \cdot \mathbf{S}_{j+1} - HS_j^z - h\,(-1)^j\, S_j^x \right]. \qquad (1)$$

The sine-Gordon quantum field theory [8–10] applied for this model predicts that the elementary excitation spectrum is to be formed by solitons and their multiple bound states (breathers) with an energy gap $\Delta \propto H^{2/3}$ formed by the first breather mode [11, 12]. Such a sine-Gordon spin model has been found to be realized in a number of compounds [13–18]. Among others, copper benzoate [13] and copper pyrimidine dinitrate [15] are the most intensively studied materials.

The predictions of the sine-Gordon theory are limited to the range of small to moderate fields. Numerical simulations based on the Density Matrix Renormalization Group (DMRG) [19] by Zhao et al. [20] have shown that when the field approaches the saturated phase the energy gap is a non-monotonous function of the field, and that it presents a minimum around the saturation field before the linear increase above saturation. This result has been understood in analytical terms somewhat later by Fouet et al. [21], who have shown, using field-theory arguments, that the gap around the saturation field in one-dimensional spin systems scales as $h^{4/5}$. This exponent is larger than the exponent that controls the gap opening at low field, and for a small enough proportionality constant between the staggered field and the external field, this leads to a local minimum of the gap around the saturation field.

These remarkable changes in the excitation spectrum in the vicinity of the saturation field ($H_{sat} \approx 27$ T) have been identified experimentally first in copper benzoate [12]. The data obtained for $H \| c$ was compared to DMRG calculations performed for this material for $H \| c''$ [20]. The results are in qualitative agreement, but the difference between experiment and theory at high field is significant, both regarding the position of the minimum and the magnitude of the gap at high fields. Since the field orientations were different in the experiment and the cal-

culation, it is not possible to decide on the data at hand whether the microscopic model of Eq. (1) can accurately describe the high-field behavior of copper benzoate (and other sine-Gordon quantum magnets), a question that has remained unanswered since then.

Recently, the ESR excitation spectrum in the quantum sine-Gordon $S = 1/2$ AF chain material copper pyrimidine dinitrate (hereafter Cu-PM) [15] had been studied in magnetic fields up to 25 T [11, 22]. A signature of soliton and three breathers, as well as specific temperature and field dependences of ESR parameters (linewidth and g-factor) beautifully confirmed the applicability of the sine-Gordon quantum-field theoretical approach for Cu-PM for $H < J/g\mu_B$. Here, we extend the range of magnetic fields used in ESR experiments up to 63 T. We report on pronounced changes in the ESR spectrum in the vicinity of the saturation field, $H_{sat} = 48.5$ T [23], clearly indicating a transition from the soliton-breather to the magnon state. Comparison of the experimental data with numerically exact DMRG results based on the microscopic model described with Eq. (1) revealed excellent *quantitative* agreement.

Experimental.— Cu-PM, $[\text{PM-Cu}(\text{NO}_3)_2(\text{H}_2\text{O})_2]_n$ (PM = pyrimidine), crystallizes in a monoclinic structure belonging to the space group $C2/c$ with four formula units per unit cell [15]. The lattice constants obtained from single-crystal X-ray diffraction are $a = 12.404$ Å, $b = 11.511$ Å, $c = 7.518$ Å, $\beta = 115.0°$. The Cu ions form chains running parallel to the short ac diagonal (Fig. 1). The Cu ions are linked by the N-C-N moieties of pyrimidine, which constitute the intrachain magnetic exchange pathway. The Cu coordination sphere is a distorted octahedron, built from an almost squarish N-O-N-O equatorial plane and two oxygens in the axial positions. In this approximately tetragonal local symmetry, the local principal axis of each octahedron is tilted from the ac plane by $\pm 29.4°$. Since this axis almost coincides with the principal axis of the g-tensor, the g-tensors for neighboring Cu ions are staggered. The exchange constant $J = 36 \pm 0.5$ K was extracted from the single-crystal susceptibility [15] and confirmed by magnetization measurements [23].

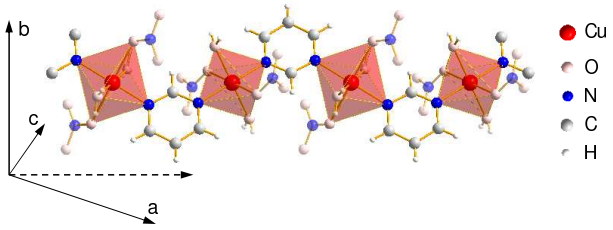

FIG. 1: (Color online) Schematic view of the crystal structure of Cu-PM, showing the alternation of octahedrons. The Cu-chains are running parallel to the short ac diagonal (denoted by the dashed arrow).

High-field ESR experiments of Cu-PM were performed at the Dresden High Magnetic Field Laboratory (Hochfeld-Magnetlabor Dresden, HLD) using a pulsed-field ESR spectrometer [24] equipped with VDI sources of millimeter-wave radiation (product of Virginia Diodes Inc.) and with a transmission-type probe in the Faraday configuration. A 8.5 MJ/70 T magnet was employed to generate pulsed magnetic fields with a pulse-field rise time of 35 ms and full-pulse durations of about 150 ms. The magnetic field was applied along the c'' direction, which is characterized by the maximal value of the staggered magnetization for Cu-PM [15]. Experiments were performed at a temperature of 1.9 K. High-quality single-crystals of Cu-PM with typical size of 3x3x0.5 mm^3 were used. 2,2-Diphenyl-1-Picrylhydrazyl (known as DPPH) was employed for the calibration of the magnetic field.

Results and discussion.— In Fig. 2, we show typical pulsed-field ESR spectra taken in Cu-PM at 1.9 K and at frequencies of 297.6 GHz, 309.6 GHz, and 400 GHz. Several very pronounced ESR modes were resolved. As mentioned above, ESR spectra in Cu-PM were previously measured in magnetic fields up to 25 T [11]. The corresponding data from Ref. [11] and results of the present pulsed-field ESR experiments are compiled in Fig. 3 using filled and open symbols, respectively. In addition to the soliton and three breather modes, additional ESR modes were observed in the magnetic excitation spectra, including the ones labeled by $C1-C3$ (which correspond to the edges of the soliton-breather continua) and the mode $U1$, which can be related to bound states due to topological edge effects [25, 26].

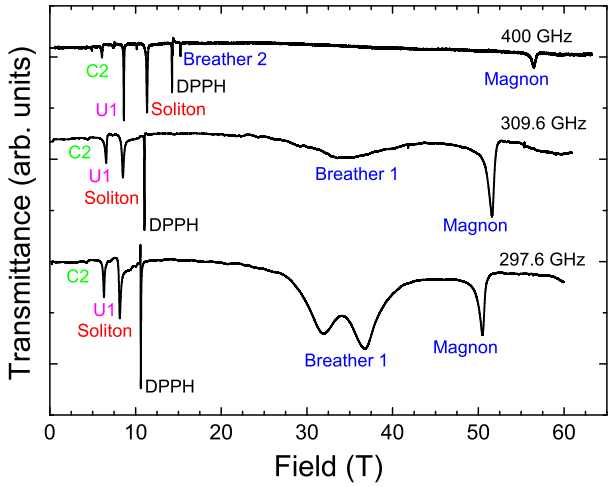

FIG. 2: (Color online) ESR transmission spectra of Cu-PM, taken at frequencies of 297.6 GHz, 309.6 GHz, and 400 GHz at $T = 1.9$ K (DPPH is used as a marker).

According to the sine-Gordon quantum field theory for

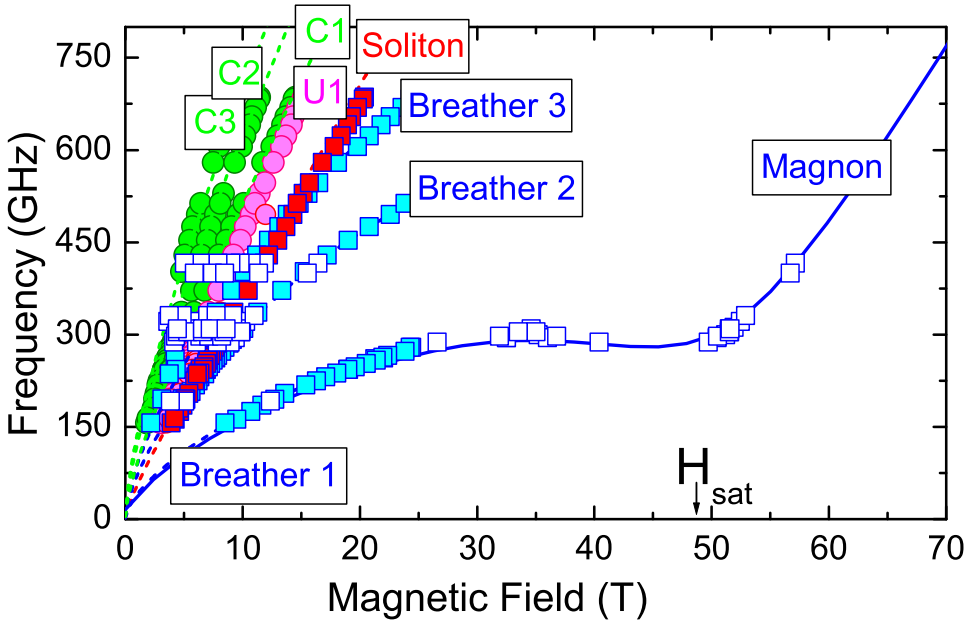

FIG. 3: (Color online) Frequency-field dependence of the detected ESR modes in Cu-PM. Experimental data are denoted by symbols, and lines correspond to the results by use of the sine-Gordon theory (dashed lines) and of the DMRG (solid line). Data denoted by closed symbols are taken from Ref. [11], while open symbols are experimental results obtained in the present study.

quantum spin-1/2 chains [9, 10], the field-induced energy gap can be calculated using the expression for the first breather excitation mode [10]:

$$\Delta_g = 2J\frac{2\Gamma(\frac{\xi}{2})v_F}{\sqrt{\pi}\Gamma(\frac{1+\xi}{2})}\left[\frac{g\mu_B H}{Jv_F}\frac{\pi\Gamma(\frac{1}{1+\xi})cA_x}{2\Gamma(\frac{\xi}{1+\xi})}\right]^{\frac{1+\xi}{2}}\sin(\pi\xi/2). \quad (2)$$

In this expression, c is the proportionality coefficient connecting the uniform applied field H and the effective staggered field $h = cH$ ($c = 0.083$ for Cu-PM [22]), the parameter $\xi = \left(2/(\pi R^2) - 1\right)^{-1}$, where R is the compactification radius, and v_F has the meaning of the Fermi velocity [10]. The amplitude A_x, which is also a function of H, has been recently computed numerically [27]. Excellent agreement between experimental data and results of the calculation using Eq. (2) for the first breather mode in magnetic fields up to 25 T was found [11].

Since the expression (2) is valid for a wide range of fields but only up to $H \sim J/g\mu_B$, it is necessary to turn to another approach to calculate the spin gap in the microscopic model of Eq. (1) at high fields ($H > J/g\mu_B$). To this end, we have performed DMRG calculations directly for the model of Eq. (1) since this numerical technique is very accurate for all fields. The results of the DMRG calculations for the field-induced gap using the microscopic model described by Eq. (1) with $L = 200$ lattice sites and $c = 0.083$ are shown in Fig. 3 by a solid line. These results were obtained by performing up to 10 DMRG sweeps and keeping up to $m = 500$ states, resulting in a discarded weight $\varepsilon \ll 10^{-10}$. Note that due to the presence of the transverse-field term in the Hamiltonian (1), $S^z_{\rm total}$ is not a good quantum number, limiting the possible system sizes. However, already for the system size shown, the results for the gap are essentially the same as in the thermodynamic limit, as revealed by comparing with smaller systems. Several remarks are in order. First of all, the DMRG results are in very good agreement with the prediction of the sine-Gordon theory in its limit of validity (low field). Secondly, and more importantly, the agreement between the DMRG results and the experimental results is excellent at all values of the field, in particular up to H_{sat} and above. This establishes that the microscopic model of Eq. (1) provides a quantitative description of the spin-gap behaviour in spin-1/2 sine-Gordon chains for all values of the field.

Now that the validity of the theoretical description has been established, let us comment on the physical mechanism behind the non-monotonic increase of the gap [20, 21]. In the absence of a staggered field, the system is gapless below $H = H_{sat}$, and it is in the fully

spin-polarized state above. In that state, elementary excitations are magnons, and the gap opens linearly with $H - H_{sat}$. The presence of a staggered field perpendicular to the external field opens a gap in the spectrum because it breaks the rotational symmetry around the field. Now, the impact of the staggered field is related to the magnitude of the transverse magnetization it induces. Close to saturation, the spins are almost polarized, and the system cannot develop a large transverse staggered magnetization. So the staggered field is less efficient to open a gap close to saturation than at low field. This is the basic mechanism behind the different scalings of the gap with c at low field ($\Delta \propto c^{2/3}$) and close to saturation ($\Delta \propto c^{4/5}$). For small enough c, this leads to a minimum of the gap around the saturation field. This explains the small but still well-resolved dip in the frequency-field dependence of magnetic excitations in Cu-PM in the vicinity of H_{sat}. Such a behavior appears to be a general feature of the high-field excitation spectrum of quantum spin-1/2 chain systems with alternating g-tensor and/or Dzyaloshonskii-Moriya interactions.

Summary.— We have presented a detailed ESR studies of Cu-PM, a material containing $S = 1/2$ AF chains with alternating g-tensor and DM interaction, and exhibiting a field-induced gap. From that we extracted the field-dependent ESR excitation spectrum of Cu-PM in magnetic fields up to 63 T. The field-induced change in the gap behavior was observed directly, clearly indicating the effect of a suppression of the soliton-breather magnetic-excitation regime by a strong magnetic field followed by a transition into the fully spin-polarized phase with magnons as elementary excitations. By comparing the entire set of data with results of DMRG calculations (based on parameters obtained earlier [11, 22]) the validity of the used theoretical approach has been proven. Excellent agreement between the experiment and results of the calculations was found. Our results are relevant for the understanding of the spin dynamics in copper benzoate and other $S = 1/2$ Heisenberg antiferromagnetic chain systems.

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