Magnetic properties of the $S = \frac{1}{2}$ Heisenberg spin-chain material (6MAP)CuCl$_3$

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Abstract. Magnetic properties of the $S = \frac{1}{2}$ Heisenberg spin-chain material (6MAP)CuCl$_3$ have been probed by means of magnetization, specific-heat and electron spin resonance (ESR) measurements. A pronounced low-temperature Curie-like tail in the magnetic susceptibility was found at low temperatures. As recently suggested, such a behavior could originate from staggered magnetization effects, responsible also for the field-induced gap opening in $S = \frac{1}{2}$ chains with broken translational symmetry. We found a clear anomaly in the specific heat having a broad maximum at $T_{\text{max}} \sim 2.3$ K, accompanied by a significant ESR line broadening and $g$-factor shift. The specific-heat anomaly is magnetic-field independent, indicating that its origin is not related to the field-induced transverse staggered magnetization effects.

Recently, low-dimensional spin systems have received a considerable amount of attention. Quantum fluctuations, significantly enhanced in spin systems with reduced dimensionality, give rise to a variety of strongly correlated states and make low-dimensional magnets an ideal tool for testing various theoretical concepts. To understand the role of quantum fluctuations in strongly correlated electron and spin systems with reduced dimensionality, it is important to explore its phenomenology in simple and well-controlled model systems. An isotropic $S = \frac{1}{2}$ Heisenberg antiferromagnetic (AFM) chain with uniform nearest-neighbor exchange coupling represents one of the most fundamental models of quantum magnetism. Its ground state is a spin singlet, and the dynamics are determined by a gapless two-particle continuum of spin-$\frac{1}{2}$ excitations, commonly referred to as spinons. A uniform external magnetic field causes a substantial rearrangement of the excitation spectrum, making the soft modes incommensurate [1, 2], although the spinon continuum remains gapless. Since the $S = \frac{1}{2}$ AFM chain is critical, even small perturbations can considerably change fundamental properties of the system. In this context, understanding the nature of the ground state and excitations in quantum spin chains is an important challenge.

The crystallographic structure of the spin $S = \frac{1}{2}$ chain complex (C$_6$H$_9$N$_2$)CuCl$_3$ [hereafter (6MAP)CuCl$_3$] is orthorhombic with space group $Pmna$ and lattice constants $a = 11.4$ Å, $b = 6.6$ Å, and $c = 12.8$ Å at room temperature [3]. Crystallographically, the compound consists of $S = \frac{1}{2}$ chains running along the $b$ direction. The individual chains are effectively isolated in the $a$ and $c$ directions by the (C$_6$H$_9$N$_2$)$^+$ cations. Based on the analysis of the crystal structure and magnetization, the low-dimensional nature of the magnetic interactions in (6MAP)CuCl$_3$
has been revealed in previous works [3, 4]. However, low-temperature features in this compound are overshadowed by a pronounced low-temperature Curie tail, which cannot be explained by a simple $S = \frac{1}{2}$ Heisenberg AF chain model. As recently shown by Feyerherm et al. [5], staggered-magnetization effects originating from broken translational symmetry (e.g. due to an alternating $g$-tensor and/or Dzyaloshinskii-Moriya interaction) in $S = \frac{1}{2}$ chains can result in such behavior. In the presence of these effects, the application of a uniform external field $B$ induces an effective transverse staggered field $h \propto B$, which leads to the opening of an energy gap $\Delta \propto B^{2/3}$. In the present paper the magnetic properties of the $S = \frac{1}{2}$ Heisenberg system (6MAP)CuCl$_3$ were tested using magnetization, specific-heat, and ESR techniques.

Magnetization measurements of single-crystalline samples of (6MAP)CuCl$_3$ were performed using a Quantum Design SQUID magnetometer in the temperature range of 1.8 - 300 K. The magnetization measured as a function of temperature in a magnetic field of 0.1 T parallel and perpendicular to the $b$ axis is shown in Fig. 1. For both crystal orientations, $\chi$ exhibits a broad peak at $\sim$ 70 K (which is a signature of the low-dimensional character of the magnetic interactions) and a Curie-like upturn is observed below $\sim$ 15 K. Overall, the data are similar to those measured by Liu et al. [3] in a field of 5 T. In addition, we performed the magnetization measurements vs magnetic field at temperatures of 1.8, 15, and 70 K. The magnetization exhibits a linear field dependence measured in fields up to 7 T. Furthermore, no saturation of the magnetization was observed in pulsed fields up to 60 T, measured at temperatures down to 1.5 K.

The low-frequency ESR experiments were done using an X-band Bruker E 500 spectrometer operating at a frequency of 9.4 GHz. The ESR spectra appear as a single resonance line with a shape close to Lorentzian. The angular dependences of the ESR spectra were measured in three different geometries with magnetic field in the $ab$, $bc$, and $ac$ planes (Inset of fig. 2). In contrast to the conventional angular dependencies of the $g$-factor measured in the $ab$ and $bc$ planes, the angular dependence of the $g$-factor in the $ac$ plane exhibits a more complex behavior. Such behavior can be described assuming the contribution from two magnetically inequivalent Cu chains, which is consistent with earlier observations [4]. Figure 2 shows the temperature dependence of the linewidth and the $g$-factor of (6MAP)CuCl$_3$ measured at a frequency of 73 GHz for $B \parallel b$. With decreasing temperature, the ESR line becomes broader, accompanied by a pronounced shift of the $g$-factor. In most cases, such a behavior is a characteristic feature

Figure 1. (Color online) The temperature dependence of the magnetic susceptibility, $M/H$, in (6MAP)CuCl$_3$ at $B \parallel b$ (circles) and $B \perp b$ (squares).
of enhanced short-range order correlations competing with thermal fluctuations. A significant $g$-factor shift and ESR line broadening was predicted [7] and confirmed experimentally [8] when approaching the soliton-breather regime in $S = \frac{1}{2}$ chains with alternating $g$-factor and the Dzyaloshinskii-Moriya interaction.

The specific heat of a (6MAP)CuCl$_3$ single crystals was measured in the temperature range 0.35 - 100 K by use of a heat-pulse method in a Quantum Design PPMS system. A relatively broad anomaly was observed at $\sim 2.3$ K (Fig. 3). The entropy under this anomaly, $\Delta S = 4$ J/molK, was calculated after subtraction of lattice contributions and the low-temperature part of the magnetic specific heat of a linear chain using a simple polynomial approach. In the case of a field-induced gap (occurring for instance in Cu-PM [5]), a significant

Figure 2. (Color online) The temperature dependences of the ESR linewidth and of the $g$-factor measured at a frequency of 73 GHz for $B \parallel b$. The inset shows the angular dependence of $g$-factor at room temperature for different orientations of the magnetic field.

Figure 3. (Color online) Temperature dependence of the specific heat of single crystalline (6MAP)CuCl$_3$ for fields of 0, 10, and 14 T, denoted by squares, circles, and triangles respectively.
shift of the anomaly with increasing higher magnetic field would be expected. Such behavior would correspond to the creation of a breather mode as shown in Ref. [6]. The specific heat of (6MAP)CuCl$_3$ was measured in magnetic fields up to 14 T. No changes in the anomaly position as well as in the overall specific heat were observed (Fig. 3). This indicates that the observed anomaly is of different origin as that corresponding to the field-induced transverse staggered-field effects.

In summary, magnetic properties of the $S = \frac{1}{2}$ Heisenberg spin-chain material (6MAP)CuCl$_3$ have been studied using magnetization, specific-heat and electron spin resonance techniques. A broad anomaly in the specific heat appears at around $\sim 2.3$ K. At around the same temperature we observed a significant ESR line broadening and $g$-factor shift. The anomaly position is independent on magnetic field, indicating that its origin is not related to the field-induced gap opening due to an effective transverse staggered magnetization. To explain the origin of the low-temperature specific-heat anomaly, tunable-frequency ESR and neutron-diffraction measurements are in progress.

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