Exploring antiferromagnetic $S = \frac{1}{2}$ dimer systems in high magnetic fields

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Abstract. We report on measurements of magnetic and thermodynamic properties on two different Cu$^{2+}$-containing S = $\frac{1}{2}$ dimer systems. One is the recently synthesized metal-organic system C$_{36}$H$_{48}$Cu$_2$F$_6$N$_8$O$_{12}$S$_2$ (TK91). At temperatures $T < 0.2$K and fields around 6T, strong enough to close the spin gap to the excited triplet state, indications for a field-induced phase transition are observed making this system a potential candidate to study the Bose-Einstein condensation of magnons. The second system is the natural mineral Cu$_3$(CO$_3$)$_2$(OH)$_2$ (azurite) which was identified as a distorted diamond chain – a realization of a 1D quantum frustrated system. We find a huge acoustic anomaly around 31T accompanying a magnetic soft mode.

1. Introduction

Low-dimensional quantum magnets, exposed to strong magnetic fields, reveal a variety of fascinating phenomena. An example of high current interest is the possibility to realize a Bose-Einstein condensation (BEC) of magnetic excitations in three-dimensionally (3D) coupled spin-dimer systems [1]. The spin singlet ground state ($S = 0$) in these systems is separated from the lowest branch ($S_z = +1$) of the excited triplet states by a spin gap $\Delta$ which decreases linearly with the field. These triplet components can be regarded as bosons (magnons) which can hop to neighboring dimers due to the transverse components of the interdimer interaction. Conversely, the longitudinal component of this interaction prevents the presence of more than one boson at a single dimer site. Thus, the system can be considered as a gas of 3D bosons with a hard-core repulsion. If the applied field is strong enough to close the spin gap and the hopping term is dominant, magnons may undergo BEC [2]. This phenomenon corresponds to a field-induced phase transition into a canted antiferromagnetic (AFM) state in the original spin system. The suggestion that BEC of magnons could be studied in coupled spin-dimer systems has stimulated extensive experimental and theoretical studies of such systems.

Another field of active research on low-D quantum magnets concerns the novel behavior arising from the interplay of strong quantum fluctuations and geometrical frustration. One of the simplest 1D quantum frustrated systems is the diamond chain. Recently, Kikuchi et al. [3] have proposed that the natural mineral Cu$_3$(CO$_3$)$_2$(OH)$_2$ (azurite), with alternating Cu$^{2+}$ monomers and dimers along the
crystallographic b-axis, represents a good realization of such a diamond chain. According to magnetic measurements, including high-field ESR [4] and magnetization studies [5], the ground state of azurite can be described as a spin fluid (SF), situated close to a quantum critical point separating the gapless SF phase from a gapped dimer state. In addition, the high-field magnetization showed a distinct plateau at one third of the saturation magnetization which is accompanied by a soft mode in the magnetic excitation spectrum [4]. These particular magnetic properties make azurite an interesting object for ultrasonic measurements which have proved a powerful spectroscopic tool at high magnetic fields [6].

In this paper, we report on the low-temperature magnetic properties of a recently synthesized 3D coupled spin-dimer system, C_{36}H_{48}Cu_{2}F_{6}N_{8}O_{12}S_{2} (TK91). Our data show indications of a field-induced phase transition at very low temperatures (< 0.2K) and at fields ~ 5.9–6.5T. The possibility of changing both the intra-dimer and inter-dimer interactions in this compound by chemical substitutions makes it a potentially good system to study BEC of magnons. In addition, we present magnetic and acoustic measurements on a high-quality single crystal of azurite. We find dramatic anomalies in the sound velocity at high magnetic fields indicating that the spin system is highly sensitive to specific ionic displacements.

2. The 3D coupled dimer system - TK91

In an attempt to search for new quantum spin systems with interesting spin topologies, we have recently synthesized novel Cu^{2+}-containing coordination polymers by using hydroquinone-derived linkers to connect the magnetic Cu^{2+} ions [7]. It has been shown that by such an approach a moderate antiferromagnetic exchange interaction \( J_1 (|J_1| / k_B \sim 10 K) \) between the Cu^{2+} ions can be achieved. More importantly, these linkers could be chemically modified to synthesize compounds with desired magnetic properties [8]. The organic compound discussed here, C_{36}H_{48}Cu_{2}F_{6}N_{8}O_{12}S_{2} (TK91), is a result of such a design strategy [7, 8]. As demonstrated in Fig. 1, the Cu^{2+} ions have distorted octahedral coordination environment and are bridged by hydroquinone linkers to form dimer units. Neighboring dimers are connected via two long axial Cu-O bonds providing a potential path for inter-dimer magnetic exchange.

![Figure 1: Schematic representation of the crystal structure of the Cu^{2+} coordination polymer TK91.](image)

The dc magnetic susceptibility \( (\chi_{dc} = M/B) \) of single-crystalline samples of TK91 was measured down to 2K using a Quantum Design SQUID magnetometer. Measurements for \( T \leq 2K \) were conducted employing an ac-susceptibility set-up adapted to a \(^3\)He-\(^4\)He dilution refrigerator. The \( \chi_{dc} \) data shown in Fig. 2 reveal a broad peak at \( T \sim 6K \), then drop and extrapolate to zero for \( T \rightarrow 0 \), suggesting the existence of a gap in the spin-excitation spectrum. As indicated by the solid line, \( \chi_{dc}(T) \)
can be fitted nicely by an isolated-dimer model with an additional Curie term to account for a small number of isolated impurity spins. From the fit, which covers also the $\chi_{dc}$ data at low temperatures (inset to Fig. 2), the value of the intradimer coupling is found to be $9.4(2)K$. The concentration of free $S = \frac{1}{2}$ impurities is estimated to be less than 1%, reflecting the high quality of the single crystals studied here.

While the susceptibility data at small fields would be compatible with a simple isolated-dimer system, measurements of the low-temperature specific heat in magnetic fields $B \geq 4$ T (not shown) revealed marked deviations from such a behavior [9]. These observations have been attributed to the presence of a significant dimer-dimer interaction [9]. In fact, clear indications for inter-dimer interactions were found also in \textit{ab initio} calculations yielding a ratio of intra- to inter-dimer couplings of 10:1 [8, 9]. According to recent quantum Monte Carlo simulations [10], a field-induced phase transition into a long-range AFM ordered state is expected for such a 3D-coupled dimer system.

To search for the magnetic ordering in TK91, we performed measurements of the magnetocaloric effect (MCE) on a single crystal in fields up to 15T in a $^3$He-$^4$He dilution refrigerator. The MCE describes the change in temperature of a magnetic material under adiabatic conditions through the application of an external magnetic field. This effect is particularly pronounced at temperatures and fields corresponding to magnetic phase transitions, and it is a powerful and widely used method for investigating the nature of these transitions. Measurements of the MCE are especially useful when other thermodynamic quantities, such as the specific heat, are not accessible because of the smallness of the available single crystals. For TK 91, the typical crystal masses are less than 1 mg. The changes of the sample temperature, $T_s$, were monitored during magnetic field sweeps at different bath temperatures. The MCE around 0.41K is plotted in Fig. 3(a). As shown in the figure, $T_s(B)$ rises when the field is swept through $B \sim 6.2$T irrespective of whether the field has been increased or decreased. To illustrate the heating process more clearly, we plot $dT_s/dB$ for the sweeping-up data in Fig. 3(b). On increasing the field, $dT_s/dB$ shows a maximum roughly at 6.5T. A similar hysteretic MCE effect was observed also in an organic compound DTN [11] and the inorganic dimer system BaCuSi$_2$O$_6$ [12]. Both systems are believed to undergo a field-induced BEC of magnons at low temperatures [11, 12]. In the case of DTN, the irreversible heating was attributed to a coupling to the lattice which may give rise to a first-order phase transition [11]. The peak in $dT_s/dB$ becomes sharper and more pronounced as the temperature decreases (see Fig. 3(b)), and yet, the position of the peak hardly changes. This
observation seems to be in conflict with the results on the above-mentioned magnetic systems, where
the peak in dT_s/dB reveals a significant temperature dependence.

Figure 3: a) Sample temperature T_s vs. field at ~ 0.4K. Solid (dotted) line corresponds to sweeping up
(down) data. Circles are \(\chi_{ac}(B)\) data taken at 0.46K. b) dT_s/dB vs. B at different temperatures.

In those experiments, the peaks in dT_s/dB were found to coincide with the positions of phase-
transition anomalies as determined from temperature-dependent measurements, and thus identified
with the transition separating the magnetic BEC state from the surrounding non-magnetic spin liquid
phase [11, 12]. In order to check whether or not TK91 undergoes a field-induced transition at all, we
have measured \(\chi_{ac}\) as a function of field at various temperatures down to 0.06K. A selection of
\(\chi_{ac}\) data are shown in Fig. 4. No hysteresis is found upon increasing and decreasing the field. At T ≥ 0.2K, the
data reveal a single broadened peak around 6.2T. Upon cooling to below about 0.2K, however, the
peak narrows significantly and two increasingly sharp features appear on its low- and high-field flank.
These results are consistent with the MCE data which, for experimental reasons, were limited to
temperatures T ≥ 0.4K. As shown in Fig. 3(a), the inflection points in the MCE curves at ~ 0.4K are
very close to the peak of \(\chi_{ac}(B)\) at 0.46K. The positions of the sharp maxima in \(\chi_{ac}(B)\) are shown in
the inset of Fig. 4 in the T-B plane. We tentatively assign these maxima as the lower and upper boundary
of a field-induced AFM ordered state. The lack of data points at T > 0.15K is due to the increasing
difficulties in determining the peak positions: with increasing temperature, the peaks move closer
together, become reduced in size, and eventually merge with the broadened maximum in the centre.
Since a broad peak in \(\chi_{ac}(B)\) is visible even up to temperatures above 1K, where the weak inter-dimer
interactions should become irrelevant, this feature is not related to the field-induced phase transition
but rather reflects the thermally smeared change in the magnetization across the saturation field. Work
is now in progress to obtain a more accurate low-temperature phase diagram of TK91 and to explore
in detail the possibility to study BEC of magnons under variable conditions in this material.
3. The frustrated distorted diamond chain - azurite (Cu$_3$(CO$_3$)$_2$(OH)$_2$)

The diamond chain, consisting of quasi-one-dimensional diamond-shaped units of coupled Cu$^{2+}$ (S = $\frac{1}{2}$)-containing monomers and dimers, is one of the simplest realizations of a frustrated quantum spin system. As a result of the frustration, the ground state strongly depends on the ratio of the magnetic coupling constants $J_1 : J_2 : J_3$ [13, 14]. For the general case of the distorted diamond chain ($J_1 \neq J_3 \neq J_2$, cf. Fig.5(b)), Okamoto et al. [15] explored theoretically the phase diagram at $T = 0$ which comprises a ferromagnetic phase, a dimerized phase, as well as a spin fluid phase.

Recently, Kikuchi et al. [3] have found that the natural mineral azurite is a good realization for such a distorted diamond chain. Prior to that finding, only a few investigations had been performed on this material [16-18]. These studies revealed a transition into a long-range AFM order at $T_N = 1.8$K indicating the presence of finite inter-chain interactions. Figure 5(a) shows a section of the structure projected along the c-direction. The large, light grey distorted rectangles represent the Cu-dimer units. Inside such a dimer, the Cu$^{2+}$ (S = $\frac{1}{2}$) ions are antiferromagnetically coupled via oxygen atoms (dark grey bowls). The small, dark grey rectangles are the Cu-monomers, connecting the dimers along the b-axis. The single crystals of azurite studied here were supplied by the Institute of Mineralogy at the University of Frankfurt. The samples for the various measurements were cut out of a large high-quality crystal. The temperature dependence of the magnetic susceptibility is displayed in Fig. 6 in the temperature range from 300K to 2K. The data were taken utilizing a Quantum Design SQUID magnetometer in a field of 0.5T applied parallel and perpendicular to the b-axis. Except for a slightly enhanced overall susceptibility, our data are consistent with those reported by Kikuchi et al. [5]. This includes the broadened maxima at 23K and 5K, as well as the appearance of a small anisotropy below about 25K. The anisotropy has been attributed to the presence of a Dzyaloshinskii-Moriya interaction [5]. In Ref. [5] the susceptibility was analyzed by employing a theoretical curve obtained from a high-temperature series expansion [19]. The best fit was achieved for the antiferromagnetic coupling

![Figure 4: $\chi_m(B)$ of TK91 at various temperatures. Inset: positions of sharp maxima in $\chi_m(B)$.](image-url)
constants $|J_1/k_B| = 19K$, $|J_2/k_B| = 24K$ and $|J_3/k_B| = 8.6K$ under the constraint given by their high-field magnetization measurements, yielding a ratio of the coupling constants $J_1 : J_2 : J_3$ to $1: 1.25 : 0.45$.

Figure 5: Schematic representation of the crystal structure of azurite (a) and definition of magnetic exchange interactions (b).

According to their results, the ground state of azurite is in the spin fluid phase close to the quantum phase transition which separates this state from the dimerized phase, consistent with previous high-field ESR measurements [4]. By fixing the relative size of the coupling constants to the ratio given above, the best fit of the high-temperature series expansion to the susceptibility data in Fig. 6, for temperatures from $300 - 45K$, yields antiferromagnetic coupling constants $|J_1/k_B| = 18.2K$, $|J_2/k_B| = 22.75K$, and $|J_3/k_B| = 8.19K$ (and $g = 2.135$), in full accordance with the results of Ref. [5].

Figure 6: $\chi_{mol}(T)$ of azurite for fields parallel (solid circles) and perpendicular (open squares) to the diamond chain direction. The solid line is a fit based on a high-T series expansion [19]. The inset shows the low-temperature part of $\chi_{mol}(T)$.

The inset of Fig. 6 displays the low-T part of $\chi(T)$ measured in a dilution refrigerator down to 0.06K. $\chi(T)$ is decreasing down to 1.85K where a sharp kink is visible indicating the onset of long range AFM order. The Curie-like upturn at low temperatures corresponds to a concentration of $S = \frac{1}{2}$ impurities of only $\sim 0.2\%$ reflecting the high quality of the crystal studied here.
Turning now to the high-field behavior, we show, in Fig. 7, relative changes of the longitudinal elastic mode $c_{22}$ propagating along the b-axis as a function of field $B \parallel b$ at various temperatures. At 9.75K, the data reveal a pronounced minimum around 31T. This softening proceeds upon further cooling to 4.2 and 3.5K, giving rise to a huge minimum in $\Delta c_{22}$, the position of which remains virtually unchanged. The combination of this drastic softening and the accompanying strong attenuation makes it very difficult to trace the effect for temperatures below 3.5K. The shape of the sound velocity anomaly and the absence of any temperature dependence in the position of the $\Delta c_{22}$ minimum are typical for a resonant interaction between the sound wave and the magnetic excitations.

![Figure 7: Field dependence of the longitudinal elastic mode $c_{22}$ at various temperatures.](image)

A similar observation was made for the 2D coupled-dimer system SrCu$_2$(BO$_3$)$_2$ [20], where pronounced anomalies were found to accompany magnetic soft modes giving rise to the formation of plateaus in the magnetization. In fact, according to the high-field ESR measurements by Otha et al. [4], a soft mode behavior can be expected in azurite around 30T. In their ESR measurements, they were able to trace the corresponding resonance (C) down to a frequency of about 50GHz, i.e. 26T. The present acoustic measurements, performed at a frequency of 60MHz, complement the ESR data to the low-frequency range and indicate a complete softening of this mode around 31T. In Fig. 8 we show a blow up of $c_{22}$ data for fields up to 27T. For this field range, i.e. below the onset of the huge softening, the field dependence of the $c_{22}$ mode could be monitored also at low temperatures down to 1.2K. For temperatures $T \leq 1.85$K, we find a sharp, step-like anomaly slightly above 10T, which shows only a small shift with increasing temperature. The origin of this anomaly is unclear at present, but may be related to the AFM phase. The field range between 16 and 26T, indicated by the two dotted lines in Fig. 8, marks the region where the one-third magnetization plateau occurs for $B \parallel b$ [5]. As the figure demonstrates, the plateau formation is accompanied by a moderate softening of the $c_{22}$ elastic constant. The pronounced acoustic anomalies, observed in azurite at high fields, indicate a significant spin-phonon interaction in this material. As for the various other Cu$^{2+}$-containing low-D spin systems, where similarly pronounced anomalies have been observed [6, 20], the spin-phonon interaction is of exchange-striction type, arising from the strain dependence of the exchange coupling constant. From
the enormous size of the effect, a large Grüneisen parameter can be inferred which may result from the proximity of the system to a quantum critical point [21].

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