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Thermal expansion of the spin-$\frac{1}{2}$ Heisenberg-chain compound $Cu(C_4H_4N_2)(NO_3)_2$

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Abstract. Compounds containing magnetic subsystems representing simple model spin systems with weak magnetic coupling constants are ideal candidates to test theoretical predictions for the generic behavior close to quantum phase transitions. We present measurements of the thermal expansion and magnetostriction of the spin-$\frac{1}{2}$-chain compound copper pyrazine dinitrate $Cu(C_4H_4N_2)(NO_3)_2$. Of particular interest is the low-temperature thermal expansion close to the saturation field $H_c \simeq 13.9\,\mathrm{T}$, which defines a quantum phase transition from the gapless Luttinger liquid state to the fully saturated state with a finite excitation gap. We observe a sign change of the thermal expansion for the different ground states, and at the quantum critical point H_c the low-temperature expansion approaches a $1/\sqrt{T}$ divergence. Thus, our data agree very well with the expected quantum critical behaviour.

Copper pyrazine dinitrate $Cu(C_4H_4N_2)(NO_3)_2$ (or CuPzN) crystallizes in an orthorhombic structure with lattice constants $a = 6.712\,\text{Å}$, $b = 5.142\,\text{Å}$ and $c = 11.732\,\text{Å}$, space group $Pmna$. The structure consists of linear Cu-pyrazine-Cu-chains along the a axis. [1] By zero-field susceptibility and specific heat measurements it could be shown, that CuPzN is a $S = 1/2$ chain with an antiferromagnetic (AFM) intrachain exchange constant of $J/k_\mathrm{B} \simeq 10.6\,\mathrm{K}$. [2] Recent zero-field muon-spin relaxation measurements provide evidence for long-range magnetic order below $T_\mathrm{N} \simeq 100\,\mathrm{mK}$, which implies a ratio of interchain to intrachain coupling of $J'/J \simeq 4.4 \cdot 10^{-3}$. [3] This means, that the spin chains are well isolated from each other and CuPzN very well realizes the model of a one-dimensional spin-1/2 Heisenberg chain antiferromagnet. This theoretical model is of particular interest because it represents a so-called spin Luttinger liquid (LL) with a continuous two-spinon excitation spectrum. For a finite magnetoelastic coupling, however, any AFM spin-1/2 chain is expected to show a Spin-Peierls transition, which transforms the LL to a dimerized phase with a finite excitation gap. Apparently, the magnetoelastic coupling in CuPzN is low enough to prevent such a Spin-Peierls transition for $T > T_\mathrm{N}$. Because $k_\mathrm{B}T_\mathrm{N} \ll J$, CuPzN is ideally suited for experimental studies of the LL state over a wide range of temperature and due to the relatively low value of J it also allows one to study the magnetic-field influence over a wide field range. The zero-temperature quantum phase transition from the LL phase to the fully spin-polarized high-field phase with a finite spin gap is expected to occur at $H = 2J/g\mu_\mathrm{B} \sim 15.8$ T, which is accessible in typical superconducting laboratory magnets. On approaching this quantum critical point, highly anomalous temperature dependencies of various thermodynamic properties are expected [4, 5] and have been observed recently in the related spin-1/2-ladder compound $(C_5H_{12}N)_2CuBr_4$. [6, 7, 8] In this report, we present high-resolution measurements of the thermal expansion $\alpha(T, H)$ and the magnetostriction in magnetic fields up

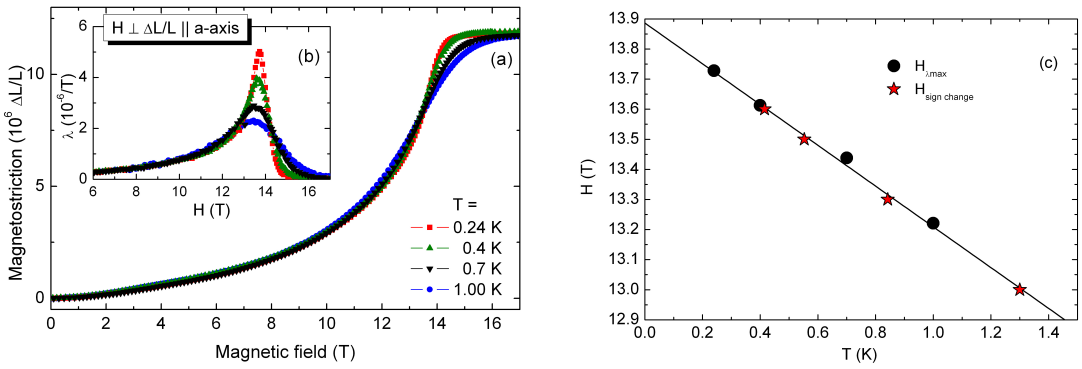

Figure 1. (a) Magnetostriction $\varepsilon = \Delta L(H)/L_0$ and (b) its field derivative $\lambda = \partial\varepsilon/\partial H$ measured along the spin chains. (c) Determination of $H_c^{\|b}(T=0)$ via a linear extrapolation of the peak positions ($\bullet$) of λ and the points ($\star$) where $\alpha(T,H)$ changes sign (see text).

to 17 T. For both zero field, as well as the quantum critical field, our data well agree with the theoretical expectations, namely $\alpha(T, H=0)$ scales with the calculated magnetic specific heat while for the critical field it shows a power-law divergence $\alpha(T, H=H_c) \propto -1/\sqrt{T}$.

The magnetostriction and thermal expansion was measured in a home-built capacitance dilatometer, which is attached to a ^{3}He insert ($T_{\rm min} \simeq 250$ mK) of a ^{4}He bath cryostat equipped with a superconducting magnet ($H_{\rm max} = 17$ T). The dilatometer can be rotated with respect to the magnetic-field axis such that the field can be aligned in any angle with respect to the measured uniaxial length change $\varepsilon(T,H) = \Delta L(T,H)/L_0$. For magnetostriction (thermal expansion) measurements T (H) is kept fixed while H (T) is continuously varied. $\Delta L(T,H)$ is measured with respect to the length at $H=0$ ($T = T_{\rm min}$) and L_0 is the total length of the sample. The derivatives $\lambda = \partial\varepsilon/\partial H$ and $\alpha = \partial\varepsilon/\partial T$ are obtained numerically. The sample studied here is from the same batch as those used in Ref. [9]. We measured the length changes parallel to the spin chains, i.e. parallel to the a axis, on a crystal with $L_0 = 2.6$ mm and the perpendicular dimensions $b \times c \simeq 0.4 \times 0.7$ mm^2. The magnetic field was oriented along the b axis, which has the largest g factor ($g_b = 2.27$ [2]) in order to minimize the critical field $H_c^{\|b} \simeq 13.9$ T.

Figure 1(a) shows the magnetostriction at various temperatures as a function of field, which strongly resembles the behaviour of the low-temperature magnetization [2]. With increasing field the sample continuously elongates and finally reaches a plateau above the saturation field. Qualitatively, this magnetostriction can be explained as follows: as the magnetic field forces the spins to orient parallel, the lattice distorts in a way to decrease the AFM coupling J. This reduces the cost in exchange energy, but causes an additional cost in elastic energy. Because, in lowest order, the first (second) term is linear (quadratic) in the distortion, such a magnetostriction always occurs. In the present case, J is minimized by increasing the distance between neighboring spins, which appears rather natural, but there are also cases where the magnetostriction has the opposite sign [11]. The uniaxial pressure dependence of J is related to the saturation value of the magnetostriction $\varepsilon_s(H > H_c) \simeq 1.2 \cdot 10^{-5}$ via $\partial J/\partial p_a = \mathcal{D}^{-1} \cdot \varepsilon_s \, V_{\rm fu}$. Here, p_a means pressure along a, $\mathcal{D} \simeq 0.69$ is the field-induced change of the spin corellator and $V_{\rm fu} \simeq 203$ Å^3 is the volume per formula unit. [7, 10] This yields $\partial \ln J/\partial p_a \simeq 2.4$ %/GPa.

As shown in Figure 1(b) the field derivative λ has a rather sharp peak, which systematically broadens and shifts towards lower field with increasing temperature. The peak positions are plotted as a function of temperature in Figure 1(c) and a linear fit extrapolates to the zero-temperature critical field $H_c^{\|b} \simeq 13.9$ T. This method to determine the QCP has already been used in the spin-ladder system $(C_5H_{12}N)_2CuBr_4$. [7]

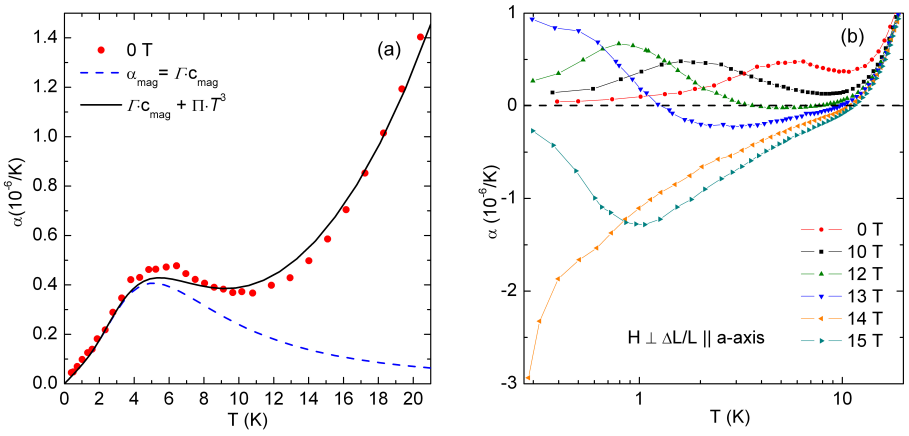

Figure 2. Thermal expansion along the spin chains measured in $H = 0$ and $H \leq 15$ T; note the logarithmic T scale in (b). The solid line in (a) is the sum of the scaled magnetic specific heat of a Heisenberg chain (dashed) and a phononic T^3 term (see text).

Figure 2(a) displays the zero-field $\alpha(T)$ showing a maximum around 6 K and a strong increase above 11 K. The latter is the phononic thermal expansion ($\alpha_{\rm ph}$), while the maximum is of magnetic origin ($\alpha_{\rm mag}$). As the Heisenberg chain contains only one energy scale J, a Grüneisen scaling between the magnetic contribution $c_{\rm mag}$ of the specific heat and $\alpha_{\rm mag}$ is expected, i.e. $\alpha_{\rm mag}(T) = \Gamma \cdot c_{\rm mag}(T)$ [4, 12]. Using the result of $c_{\rm mag}(T)$ for the Heisenberg chain [13], and assuming the usual $\alpha_{\rm ph} \propto T^3$ of acoustic phonons, we can model the measured thermal expansion $\alpha = \Gamma c_{\rm mag}(T) + \Pi T^3$ by adjusting Γ and Π as free parameters. With $\Gamma = \partial \ln J / \partial p_a = 1.7$ %/GPa and $\Pi = 1.5 \cdot 10^{-10}$/K^4, we obtain the solid line in Figure 2(a), which nicely describes the experimental data up to 20 K and the corresponding $\alpha_{\rm mag}$ is given by the dashed line. Obviously, the low-temperature expansion $\alpha(T < 4$ K) of CuPzN is of almost purely magnetic origin. The fact that this pressure dependence amounts only to about 2/3 of the value obtained from the magnetostriction data, is most likely due to the uncertainty of the phononic background, but does not affect the following discussion [10].

Figure 2(b) gives an overview of the thermal expansion data up to 15 T. With increasing field the maximum of α shifts to lower temperature and above 10 T its amplitude increases on further approaching the critical field $H_c^{\|b} \simeq 13.9$ T. For a slightly higher field of 14 T, however, the thermal expansion is completely different; $\alpha(T)$ is negative in the entire low-T range and monotonically decreases down to the lowest temperature. For an even higher field of 15 T, $\alpha(T)$ finally shows a minimum around 1 K.

Figure 3 gives a detailed view on the field region around the QCP. As shown in panel (a), the $\alpha(T)$ curves systematically change their curvature from an upward to a downward bending when the magnetic field is increased from 13.3 T to 14.1 T. From this figure alone, the location of the QCP is not obvious. Note, however, that only the $\alpha(T)$ curves for 10 T $< H <$ 13.7 T show a sign change as a function of T; see also Figure 2(b). Interestingly, the points where $\alpha(T^\star, H^\star) = 0$ match the line obtained from the maximum positions of the $\lambda(T, H)$ curves, see Figure 1(c), and thus their linear extrapolation to zero temperature also yields $H_c^{\|b} \simeq 13.9$ T. For $H > 14.2$ T, the $\alpha(T)$ curves show minima, whose positions shift to higher T with increasing field; see Figure 3(b). In Figure 3(c), we compare the three curves closest to the QCP on double-logarithmic scales. Moreover, a power-law fit of the 13.9 T curve is shown, which yields $\alpha(T, 13.9\ {\rm T}) \propto T^{-0.51}$, in almost perfect agreement with the expected $1/\sqrt{T}$ divergence.

From the above analysis, one may expect the occurrence of sign changes (minima) in $\alpha(T, H)$

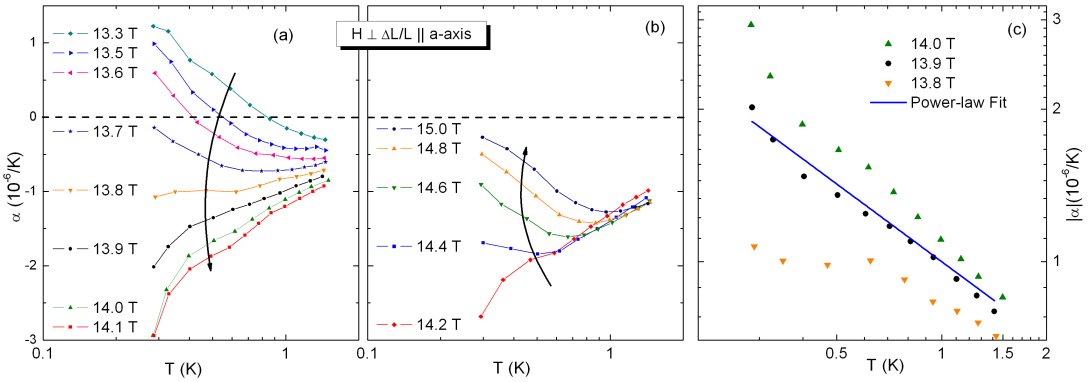

Figure 3. Thermal expansion along the spin chains for fields close to $H_c \approx 13.9\,\mathrm{T}$. The line in (c) is a power-law fit yielding $\alpha(T, 13.9\ \mathrm{T}) \propto T^{-0.51}$ (see text).

at temperatures below our minimum T for the curves measured in fields between $H_c^{\|b}$ and 13.7 T (14.2 T). Because of the AFM ordering, however, this behaviour will be definitely cut off at $T_\mathrm{N} \simeq 100\,\mathrm{mK}$, as it has been also observed in $(C_5H_{12}N)_2CuBr_4$ [8, 14, 15]. In any real material, the question how well defined the QCP is, will depend on such imperfections and also on the sample quality. As discussed in Ref. [7], however, due to a magnetic correction of the elastic moduli the quantum critical behavior may be cut off even in a 'perfect' sample at low enough temperature by a first-order phase transition.

In conclusion, we have measured the low-temperature magnetostriction and the thermal expansion along the spin-1/2 chain direction of $Cu(C_4H_4N_2)(NO_3)_2$ up to magnetic fields strong enough to induce the quantum phase transition from the Luttinger liquid phase to the fully spin-polarized state. Using a Grüneisen relation, our zero-field expansion data are well described by the spin-1/2 Heisenberg chain hamiltonian. With increasing field the experimental data follow the behaviour expected on approaching a quantum critical point. In particular, we observe the expected sign change and the $1/\sqrt{T}$ divergence of the thermal expansion.

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