Magnetic cooling through quantum criticality

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Abstract. We report measurements and theoretical calculations of the magnetocaloric properties of low-dimensional spin-1/2 antiferromagnets close to their magnetic field-induced quantum critical points. We demonstrate that the accumulation of entropy around the quantum critical point, giving rise to a critically enhanced magnetocaloric effect $\Gamma_B$, can be used for realizing a very efficient low-temperature magnetic cooling.

1. Introduction
Magnetic refrigeration provides an interesting alternative to standard cooling technologies with potential applications covering wide ranges of temperature [1]. It is based on the magnetocaloric effect (MCE) which describes temperature changes of a material in response to an adiabatic change of the magnetic field. The MCE, which is intrinsic to all magnetic materials in which the entropy $S$ changes with magnetic field $B$, has been widely used for refrigeration in the sub-Kelvin temperature range [2], including space applications [3,4], where paramagnetic salts have been the materials of choice due to their large $\Delta S/\Delta B$ values.

Here we demonstrate that the critically enhanced MCE around a $B$-induced quantum critical point (QCP) – a zero-temperature phase transition – can be used for realizing an efficient low-temperature magnetic cooling. To this end we summarize recent results of the MCE near the saturation field $B_s$ of a Cu$^{2+}$-containing coordination polymer $[\text{Cu}(\mu-C_2O_4)(4\text{-aminopyridine})(H_2O)]_n$ [5], which is a very good realization of a spin-1/2 antiferromagnetic Heisenberg chain – one of the simplest quantum-critical systems. We compare these results with the magnetothermal response of Cs$_2$CuCl$_4$, a layered triangular-lattice Heisenberg antiferromagnet with significant magnetic frustration.

A QCP is reached upon tuning an external parameter $r$ such as pressure or magnetic field to a critical value. Although the critical point is inaccessible by experiment, its presence can significantly affect the properties of the material in a wide range of temperatures. This manifests itself in anomalous power laws of thermodynamic properties as a function of temperature and, even more drastically, in an extraordinarily high sensitiveness of these properties against variations of the tuning parameter [6,7]. Upon approaching a pressure-induced QCP, for example, the thermal expansion coefficient $\alpha \propto \partial S/\partial p$
is more singular than the specific heat $C = T \cdot \partial S / \partial T$, giving rise to a divergent thermal Grüneisen parameter $\Gamma_p \propto \alpha / C$ [6,8]. Likewise for a $B$-induced QCP, a diverging magnetic Grüneisen parameter $\Gamma_B = -C^{-1}(\partial S / \partial B)_T$ is expected [6,7,9] and has recently been observed [10]. Unlike $\Gamma_p$, however, which requires the determination of the critical contributions of the two quantities $\alpha$ and $C$, $\Gamma_B$ can be determined directly via the MCE by probing temperature changes of the material in response to changes of the magnetic field $B$ under adiabatic conditions,

$$\Gamma_B = \frac{1}{T} \left( \frac{\partial T}{\partial B} \right)_S = -\frac{1}{C_B} \left( \frac{\partial S}{\partial B} \right)_T$$

(1)

2. The model system CuP – a realization of a spin-1/2 antiferromagnetic Heisenberg chain

For the proof of principle we have used the Cu$^{2+}$-containing coordination polymer $[\text{Cu}(\mu-C_2O_4)(4\text{-aminopyridine})_2(H_2O)]_n$, CuP in short, first synthesized by Castillo et al. [11]. As demonstrated in refs. [5,12,13], this material is in fact a very good realization of a spin-1/2 antiferromagnetic Heisenberg (AFHC) chain with a small intra-chain magnetic coupling constant $J / k_B = (3.2 \pm 0.1)$ K, and a correspondingly small saturation field $B_s = 4.09$ T (for $B || b$-axis), given by $g \mu_B B_s = 2J$, with $g$ the spectroscopic $g$ factor and $\mu_B$ the Bohr magneton. Since at $T = 0$, $B_s$ of the spin-1/2 AFHC marks the endpoint of a quantum critical line, a critically enhanced MCE and thus pronounced magnetic cooling effects are expected around $B_s$ for temperatures $T < J / k_B$ [9].

![Figure 1. Experimental results (symbols) and model calculations (lines) of (a) the magnetic Grüneisen parameter $\Gamma_B$ as a function of magnetic field at $T = 0.32$ K for $B || b$-axis and (b) the sample temperature $T_s$ after demagnetizing a collection of CuP single crystals under near adiabatic conditions from three different values of the initial temperature $T_i$, cf. refs. [5,13].](image)
dilution refrigerator. In the step-like technique employed [14], the sample is initially held at a temperature $T$ and a magnetic field $B$. A very weak coupling to the thermal bath ensures quasiadiabatic conditions. After applying two subsequent field steps of $+\Delta B$ and $-\Delta B$, with $|\Delta B| = 0.02$ T, sufficiently separated in time to allow the system to relax to the bath temperature, the temperature response of the sample $\Delta T$ is determined from an equal-areas construction [14].

The so-derived $\Gamma_B$ shows negative values for $B < B_s$, implying that here cooling is achieved through magnetization. Upon increasing the field, $\Gamma_B$ passes through a weak minimum, changes sign, and adopts a pronounced maximum above 4 T. Since $\Gamma_B$ is proportional to $(\partial S/\partial B)_T$ (cf. equ. (1)), the sign change implies the presence of a distinct maximum in $S_T$ around $B_s$ – a clear signature of a nearby QCP [7]. It reflects the accumulation of entropy due to the competing ground states separated by the QCP. The deviations from the theoretical calculations indicate the presence of small disturbing interactions such as a finite Dzyaloshinskii-Moriya interaction or weak inter-chain couplings [5].

To explore the potential of the enhanced MCE for magnetic cooling, demagnetization experiments were carried out under near adiabatic conditions with the sample set to the initial parameters $B_0$ and $T_0$. Figure 1b shows three cooling curves obtained by decreasing the field with a rate $\Delta B/\Delta t = 0.3$ T/min for $B \geq 6$ T and $-0.5$ T/min for $B < 6$ T. Near ($B_s$, $T$) the cooling process is almost linear in $B$ as is known from simple paramagnets where $T/B = \text{const}$. However, with decreasing temperature, the process becomes superlinear. This enhanced cooling effect, which is in accordance with the model calculations for the ideal system (broken lines in Fig. 1b), is a direct manifestation of quantum criticality. Calculations of the parasitic heat flow for this experiment indicate that a further reduction of the minimum temperature from 0.179 K to about 0.132 K could be obtained for an improved thermal isolation of the system [5,14]. These calculations imply that the main source for the deviations from the theoretical expectations lies in the presence of the above-mentioned perturbing interactions. The good agreement with the theory curves at higher temperatures, where these interactions are irrelevant, however, indicate that for a better realization of a spin-1/2 AFHC, cooling to much lower temperatures should be possible.

3. The effect of frustrating interactions – the case of Cs$_2$CuCl$_4$

The above-mentioned experimental and theoretical results on the spin-1/2 AFHC have enabled a proof-of-principle demonstration of magnetic cooling through quantum criticality. However, extensions of this concept are obvious [5] and should be further explored. As one of the promising routes in the search for materials with further improved cooling performance, the combination [5,9] of reduced dimensionality with geometric frustration [15] has been proposed. As a consequence of the frustration, a large absolute variation of the entropy with magnetic field and hence a large $\partial T/\partial B$ can be expected. As a first step in this direction, we have studied the magnetothermal response of Cs$_2$CuCl$_4$, a layered triangular-lattice Heisenberg antiferromagnet. In this material, the frustration effects derive from a dominant antiferromagnetic exchange coupling $J/k_B = 4.3$ K [16] along the in-plane $b$-axis and a second in-plane coupling of $J'' = J/3$ along a diagonal bond in the $bc$-plane [17]. Further couplings in this material include an inter-plane interaction $J''' \sim J/20$ as well as a small anisotropic Dzyaloshinskii-Moriya interaction $D \sim J/20$ [17]. This material has attracted much attention due to its spin-liquid properties [17-19] and its field-induced quantum phase transition at $B_c \sim 8.5$ T [17,20]. The latter separates long-range antiferromagnetic order below $T_N = 0.62$ K (at zero field) from a fully-polarized ferromagnetic state.

In Figure 2a, we show the MCE measured on single crystalline Cs$_2$CuCl$_4$ as a function of magnetic field $B || a$-axis at $T = 0.2$ K. The data reveal a change of sign in $\Gamma_B$ at $8.32$ T, reflecting the $B$-induced transition from antiferromagnetic order to the polarized state, in accordance with published data for the $B$-$T$ phase diagram [20]. While $|\Gamma_B|$ is small for $B < B_s$, indicating a reduced entropy as a consequence of the long-range ordering, $|\Gamma_B|$ is strongly enhanced for $B > B_s$ and decreases approximately as $1/B$ with increasing distance from $B_s$ in accordance with the expectation [6]. The
large variation of $\Gamma_B$ near $B_s$ indicates a pronounced maximum in $S_T(B)$ above the material's quantum critical point.

The results of a low-temperature demagnetization experiment for Cs$_2$CuCl$_4$ are shown in Figure 2b for an initial temperature around $T_i = 0.2$ K and two different values of the initial field $B_i$. While for $B_i = 9$ T a pronounced cooling effect with an approximately constant rate of $0.245$ K/T can be achieved, a $B$-dependent cooling at a smaller rate is revealed for $B_i = 10$ T. The latter observation is attributed to the opening of a field-induced gap in the fully-polarized state, accompanied by a reduction of the magnetic entropy with increasing distance from the critical field.

**Figure 2.** (a) Experimental results (symbols) of the magnetic Grüneisen parameter $\Gamma_B$ as a function of magnetic field at $T = 0.2$ K for $B \parallel a$-axis of Cs$_2$CuCl$_4$. Solid line indicates a $1/B$ dependence. (b) Sample temperature $T_s$ measured by demagnetizing the crystal under near adiabatic conditions from $T_i = 0.2$ K and two different values of the initial field $B_i$.

### 4. Magnetic cooling characteristics

For assessing the cooling performance of a magnetic material, various aspects have to be considered depending on the particular type of application. Relevant parameters include (i) the operating range, in particular the lowest accessible temperature $T_{\text{min}}$, and (ii) the "hold time" of the material. The latter quantity, which is inversely proportional to the cooling power, reflects the ability of the material to absorb heat without warming up too rapidly. For some applications, (iii) the efficiency $\Delta Q_c/\Delta Q_m$ can be of importance. Here $\Delta Q_c$ is the heat the material can absorb after demagnetization from $B_i$ to the field $B_f$, and $\Delta Q_m$ is the heat of magnetization released to a precooling stage held at a temperature $T_i$, the initial temperature of the magnetic cooling process. The ratio $\Delta Q_c/\Delta Q_m$ may be an issue for modern
multistage magnetic refrigerants, such as the ones used in space [3], where the system has to be optimized with regard to precooling requirements and weight.

As has been discussed in more detail in ref. [5], quantum critical systems are good alternatives to state-of-the-art paramagnets for those applications where a considerably large cooling power is required down to, in principle, arbitrarily small temperatures, and long hold times are needed over an extended temperature range all the way up to $T_i$.

![Figure 3](image)

**Figure 3.** Molar magnetic entropy $S_{\text{mag}}(T, B = \text{const})$ vs. $T$ calculated for the spin-1/2 AFHC with $J/k_B = 3.2$ K at an initial field $B_i = 7.14$ T (broken line) and a final field $B_f = B_s = 4.09$ T (dotted line). The path AB denotes an isothermal demagnetization process followed by an adiabatic demagnetization (path BC). While $\Delta Q_m$ corresponds to the area of the rectangle ABDEA, $\Delta Q_c$ is given by the hatched area. For comparison, the figure includes $S_{\text{mag}}(T, B = \text{const})$ for the frustrated two-dimensional triangular lattice spin-1/2 Heisenberg antiferromagnet with $J/k_B = J'/k_B = 4.3$ K at $B_i = 19.2$ T and $B_f = B_s = 14.4$ T.

In addition, the quantum critical systems excel by their very high efficiency $\Delta Q_c/\Delta Q_m$. This is due to the peculiar excitation spectrum above the quantum critical point which enables the system to absorb energy also at elevated temperatures. This contrasts with the paramagnets, where the absorption essentially occurs around the position of their Schottky anomaly, i.e., at temperatures $T$ distinctly lower than $T_i$. The efficiency can be determined from the magnetic entropy of the system $S_{\text{mag}}(T, B = \text{const})$ as a function of temperature. To this end, we show in Fig. 3 $S_{\text{mag}}$ for the spin-1/2 AFHC discussed above ($J/k_B = 3.2$ K) for an initial field $B_i = 7.14$ T and a final field $B_f = B_s = 4.09$ T. For comparison, the figure also includes $S_{\text{mag}}(T)$ for a frustrated layered triangular-lattice ($J/k_B = J'/k_B = 4.3$ K) spin-1/2 antiferromagnet. The latter results, which may serve as a first approximation for modelling the anisotropic triangular-lattice system Cs$_2$CuCl$_4$, have been taken from ref. [21].
In the cooling process indicated in Fig. 3, the materials are first isothermally magnetized (path AB, for example), and then, after thermal isolation, adiabatically demagnetized (path BC) to the final temperature $T_f$. The systems warm up along their entropy curves at the final demagnetization field $S_{\text{mag}}(T, B = B_f)$. The heat of magnetization at $T = T_i$, $\Delta Q_m = T_i \left[ S_{\text{mag}}(T_i, B_f) - S_{\text{mag}}(T_i, B_i) \right]$, and the heat that the material is able to absorb after adiabatic demagnetization, $\Delta Q = \int_{T_i}^{T_f} T \left[ \frac{dS_{\text{mag}}}{dT} \right]_{B_i} dT$, can be read off the figure. The efficiency factor $\Delta Q_c / \Delta Q_m$ amounts to 26% for the spin-1/2 antiferromagnetic Heisenberg chain and 50% for the two-dimensional triangular-lattice spin-1/2 Heisenberg antiferromagnet. This has to be compared to only 9% for the state-of-the-art spin-5/2 paramagnet Fe(NH$_4$)(SO$_4$)$_2$·12H$_2$O demagnetized from $B_i = 2$ T to $B_f = 0$, cf. ref. [5] and references cited therein.

5. Conclusions

We have performed measurements of the magnetocaloric properties of two low-dimensional spin-1/2 antiferromagnets close to their field-induced quantum critical points. The low-temperature magnetocaloric effect shows a characteristic sign change upon sweeping the magnetic field across the materials’ saturation field – reflecting an entropy maximum as a consequence of the nearby quantum critical point. Demagnetization experiments under almost adiabatic conditions reveal that the critically enhanced magnetocaloric effect can be used to realize a magnetic cooling mechanism with extraordinarily high efficiency.

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