Significant inverse magnetocaloric effect induced by quantum criticality

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The criticality-enhanced magnetocaloric effect (MCE) near a field-induced quantum critical point (QCP) in the spin systems constitutes a very promising and highly tunable alternative to conventional adiabatic demagnetization refrigeration. Strong fluctuations in the low- T quantum critical regime can give rise to a large thermal entropy change and thus significant cooling effect when approaching the QCP. In this work, through efficient and accurate many-body calculations, we show there exists a significant inverse MCE (iMCE) in the spin-1 quantum chain materials $(\text{CH}_3)_4\text{NNi}(\text{NO}_2)_3$ (TMNIN) and $\text{NiCl}_2\cdot 4\text{SC}(\text{NH}_2)_2$ (DTN), where DTN has substantial low- T refrigeration capacity while requiring only moderate magnetic fields. The iMCE characteristics, including the adiabatic temperature change ΔT_{ad} , isothermal entropy change ΔS , differential Grüneisen parameter, and the entropy change rate, are obtained with quantum many-body calculations at finite temperature. The cooling performance, i.e., the efficiency factor and hold time, of the two compounds is also discussed. Based on the many-body calculations on realistic models for the spin-chain materials, we conclude that the compound DTN constitutes a very promising and highly efficient quantum magnetic coolant with pronounced iMCE properties. We advocate that such quantum magnets can be used in cryofree refrigeration for space applications and quantum computing environments.

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I. INTRODUCTION

The magnetocaloric effect (MCE) represents a significant adiabatic temperature change of a magnet as a response to the varying external magnetic fields [1–4]. Historically, the first sub-Kelvin regime cooling was realized through adiabatic demagnetization refrigeration (ADR) [5]. Recently, low- T magnetic refrigeration has received refreshed research interest due to its important applications in space technology [6,7] and the cryofree sub-Kelvin environment for quantum computers [8]. It is of great research interest to pursue novel MCE refrigerants that provide higher cooling powers and can reach lower temperatures. Among others, the quantum spin-chain materials with enhanced MCE characterized by the universally diverging Grüneisen ratio near the quantum critical point (QCP) [9–15] has been proposed as a very promising quantum critical coolant for magnetic refrigeration [16,17] and an excellent alternative to the conventional ADR.

In most magnetic materials, the spin degrees of freedom in the system eventually “solidify” into a long-range order as it is cooled down to sufficiently low temperatures. In such magnetically ordered phase, the spin states are practically nontunable by external fields (due to the existence of giant Weiss molecular fields) and the corresponding MCE, temperature, or entropy change as a response to fields are usually negligible. Paramagnetic salts, such as $\text{CrK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ (chromic potassium alum, CPA) and $\text{Fe}(\text{SO}_4)_2\text{NH}_4 \cdot 2\text{H}_2\text{O}$ (ferric ammonium alum, FAA), etc., that host nearly noninteracting spins and do not order at very low temperatures, are widely used in ADR as a spin “gas” refrigerant [7]. It is commonly believed that the spin interactions are “harmful” for good ADR coolants, as they usually lead to magnetic ordering as T lowers and spoil the MCE properties.

Nevertheless, there is an exotic exception to this classic fate of interacting quantum spins. In low-dimensional quantum magnets [18], the quantum fluctuations can be strong enough to prevent the spins from classical ordering even at $T = 0$. One prominent case is the field-induced QCP in the correlated quantum magnetic materials. The enhanced quantum fluctuations near the QCP can significantly influence the thermodynamics in the quantum critical regime at low temperature [19]. When approaching the QCP, the spin system would experience a significant isothermal entropy change, which can be translated into a considerable temperature decrease under the adiabatic condition. Such quantum criticality-enhanced

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MCE is reflected in a diverging Grüneisen parameter [adiabatic temperature change rate; cf. Eq. (2)], $\Gamma_B \sim T^{-1/z\nu}$, under external field B , with z and ν the dynamical and critical exponents related to the universality class of the QCP [11,12]. Notably, such intriguing quantum critical phenomena in low-temperature thermodynamics also provide a sensitive probe of QCP in experiments [20].

The low-temperature thermodynamic properties of a typical one-dimensional (1D) quantum magnetic system—the spin-1/2 Heisenberg chain (HAFC)—have been intensively explored, where a pronounced MCE was predicted [9,10] and also observed in the compound $[\text{Cu}(\mu\text{-C}_2\text{O}_4)(4\text{-aminopyridine})_2(\text{H}_2\text{O})]_n$ (CuP). The lowest achievable temperature with the spin-chain coolants has no principal limitation (as long as the interchain interactions are negligible), and the high efficiency factor as well as long hold time make the spin-1/2 HAFC materials very promising quantum critical refrigerants [16,17].

Nevertheless, there is still plenty of room for further improvement of the performance of quantum magnetic refrigerants. As reported in Ref. [16], for the spin-1/2 HAFC compound CuP, one has to start from a rather high magnetic field, e.g., 7 T, significantly above the critical field $B_c \simeq 4.09$ T. In CuP, there indeed exists significant MCE in the range $B > B_c$, while in the smaller-field side, i.e., $B \in [0, B_c]$, rather weak (inverse) MCE was observed. Therefore, the generated strong magnetic fields (of 7 T) have actually not been fully exploited in the case of the spin-1/2 compound CuP. On the other hand, popular paramagnetic refrigerants are typically with high spin $S \geq 1$, as larger entropy changes are generally expected for higher spin systems. For example, CPA and FAA are with $S = 3/2$ and $5/2$, respectively, and the gadolinium gallium garnet (GGG) is even with $S = 7/2$. However, there are only a few studies of quantum spin models [13] and materials [15] with spin higher than $S = 1/2$.

In this work, we systematically investigate the inverse MCE (iMCE) properties of the $S = 1$ quantum chain models and materials with many-body simulations. Special emphases are put on two typical spin-1 HAFC materials, i.e., $(\text{CH}_3)_4\text{NNi}(\text{NO}_2)_3$ (TMNIN) and $\text{NiCl}_2\cdot 4\text{SC}(\text{NH}_2)_2$ (DTN), whose magnetothermodynamic properties can be accurately simulated by the thermal-state linearized tensor renormalization group (LTRG) approaches [21,22]. In particular, we find that the compound DTN has iMCE refrigeration capacity comparable to the MCE of the spin-1/2 HAFC material CuP, while requiring only a moderate external magnetic field of $B_c \simeq 3$ T in the cooling process, which is much smaller than the latter requires. Due to the pronounced cooling effects and excellent thermal transport properties [23] in DTN, we propose that DTN constitutes a very promising iMCE refrigerant with only a moderate magnetic field and competitive performance, very suitable for practical refrigeration applications.

The remaining parts of the article are arranged as follows. We present the spin-1 chain models, their thermal many-body simulations, and the related spin-1 materials in Sec. II. Our main results on iMCE of the spin-1 chains are shown in Sec. III, and Sec. IV is devoted to the conclusion and outlook.

II. SPIN-1 HEISENBERG-CHAIN MODEL AND MATERIALS

A. Heisenberg antiferromagnetic chain and tensor renormalization group

The $S = 1$ HAFC systems with single-ion anisotropy can be described by the Hamiltonian

$$\mathcal{H} = \sum_i [J\vec{S}_i \cdot \vec{S}_{i+1} + D(S_i^z)^2 + g\mu_B B S_i^z], \quad (1)$$

where $\vec{S}_i$ is the spin-1 operator on site i (with S_i^z its z component), J is the nearest-neighbor Heisenberg interaction, and D is the single-ion anisotropy parameter. In the Zeeman term, B is the external magnetic field, g is the electronic Landé factor, and μ_B is the Bohr magneton.

In a rather wide parameter regime [24,25], the spin-1 chain model given by Eq. (1) has a nonmagnetic ground state with finite spin gap, which can be closed by applying a magnetic field B through the field-induced quantum phase transition. In particular, for the case $D = 0$, the model in Eq. (1) reduces to the isotropic spin-1 HAFC model with the renowned Haldane gap, $\Delta \approx 0.41J$ [26–28], where the first-excited state is in a spin triplet $S = 1$ sector. The introduction of D in the spin chain can alter the size of the Haldane gap and drive the system into a trivial large- D phase through a topological quantum phase transition at $D/J = 0.93$ [29]. For $D > D_c$, the gap reopens and scales proportionally with D in the large- D limit. In addition, other off-diagonal single-ion anisotropies are found to be small in the two spin-1 chain compounds—TMNIN and DTN—considered in the present work, and we thus set them to zero in the rest of our discussion.

To simulate the finite-temperature properties and characterize the iMCE properties of the spin-1 chain materials, we employ the infinite-size LTRG method [21] in the bilayer form [22] for high-precision thermal many-body calculations down to low temperature $T/J = 0.01$. In the process of imaginary-time evolution (cooling), we retain up to $\chi = 400$ bond states (with truncation error $\epsilon \lesssim 10^{-5}$) in the matrix-product thermal density operator, which always guarantees accurate and converged thermodynamic results.

B. iMCE property and performance characteristics

Driven by external magnetic fields, the spin-1 chains in the quantum critical regime show significantly enhanced MCE. To quantitatively characterize the MCE property, we calculate the magnetic Grüneisen parameter,

$$\Gamma_B = \frac{1}{T} \left(\frac{\partial T}{\partial B} \right)_S = -\frac{1}{C_B} \left(\frac{\partial M}{\partial T} \right)_B, \quad (2)$$

with $C_B = T(\partial S/\partial T)_B$ the magnetic specific heat (under an external field B). The Grüneisen parameter Γ_B measures the temperature change rate as a response to the small variation of the external field under an adiabatic condition. In the numerator of Eq. (2) is a related differential quantity,

$$\Theta_T = \left(\frac{\partial S}{\partial B} \right)_T = \left(\frac{\partial M}{\partial T} \right)_B,$$

which measures the isothermal entropy change rate.

FIG. 1. Simulated thermal entropy $S(T)$ curves of three spin-chain materials, under different initial fields B_i and final fields $B_f = B_c$. Entropy change ΔS (indicated by the vertical red arrow) and adiabatic temperature change ΔT_{ad} (horizontal red arrow) are shown explicitly for the compound DTN. A-B-C-A constitutes a single-shot refrigeration process, and the dashed regime ACDE represents the heat absorbed from the load in the isofield CA process.

Correspondingly, when integrated over a given range of fields, e.g., $B \in [B_i, B_f]$ with B_i and B_f the initial and final (critical) fields in the iMCE process, respectively, the isothermal entropy change is

$$\Delta S(T) = \int_{B_i}^{B_f} \left(\frac{\partial S}{\partial B} \right)_T dB = \int_{B_i}^{B_f} \left(\frac{\partial M}{\partial T} \right)_B dB,$$

and the adiabatic temperature change is

$$\Delta T_{ad} = \int_{B_i}^{B_f} \Gamma_B T dB = - \int_{B_i}^{B_f} \frac{T}{C_B} \left(\frac{\partial M}{\partial T} \right)_B dB.$$

Besides the above MCE property characteristics, in practical applications the refrigeration efficiency factor η and hold time are important quantities measuring their cooling performance. The efficiency factor is defined as the ratio $\eta = \Delta Q_c / \Delta Q_m$, where $\Delta Q_c = \int_{T_f}^{T_i} T (\partial S / \partial T)_{B_f} dT$ refers to the heat absorption from load (indicated by the red shadow area ACDE in Fig. 1), and $\Delta Q_m = T_i [S(B_f, T_i) - S(B_i, T_i)]$

FIG. 2. (a) Simulated molar magnetic entropy change ΔS as a function of temperature T , for three compounds: TMNIN (gray dashed line), DTN (orange line), and CuP (blue dash-dotted line). (b) Comparison of the entropy change per Tesla, $\Delta S/B_{\max}$, for three compounds.

is the heat exchange between the material and the heat reservoir at the high temperature T_i . In multistage single-shot or continuous ADRs, the whole system must be optimized according to the precooling requirements and total weight, in which the efficiency factor is crucial [7]. In addition, the hold time—reflecting the temperature-time curve of the refrigerant in contact with the constant heat load—is another important parameter for an efficient refrigeration. The refrigerant temperature is defined as $T_S(t) = T_S(0) + \dot{Q}/C_m$, and particularly we require that the refrigerant temperature does not increase too rapidly (thus a long hold time) under a constant heat load $\dot{Q}$.

C. Spin-1 chain quantum magnets

Distinct from the spin-1/2 chains, the spin-1 HAFC system has gapped ground states [27,28] with symmetry-protected topological (SPT) order [47]. There has been continuous research interest in the investigation of the spin-1 chain materials, with some prominent examples listed in Table I. In these compounds, there exists the single-ion anisotropy term D [cf. Eq. (1)] besides the Heisenberg interaction J . In this work, we are particularly interested in the compounds TMNIN [30–33] and DTN [23,34–38], due to their very moderate

TABLE I. Some common spin-1 chain compounds and their microscopic Hamiltonian parameters, including the intrachain exchange J , uniaxial single-ion anisotropy D , the spin excitation gap Δ , the Landé factor g , and the (lower) critical field B_c . The magnets are listed in ascending order in strength of the Heisenberg coupling J .

Compound	Abbr.	J/k_B (K)	D/k_B (K)	Δ/k_B (K)	g	B_c (T)	Reference
$(\text{CH}_3)_4\text{NNi}(\text{NO}_2)_3$	TMNIN	11.7–12		4.1–4.5	2.22–2.25	3	[30–33]
$\text{NiCl}_2\cdot 4\text{SC}(\text{NH}_2)_2$	DTN	2.2	8.9	3.2	2.26	2.13 ^a	[23,34–38]
$\text{Ni}(\text{C}_2\text{H}_8\text{N}_2)_2\text{NO}_2\text{BF}_4$	NENB	44.8–47.7	7.5	17.4	2.14	9–13	[15,39]
$\text{Ni}(\text{C}_2\text{H}_8\text{N}_2)_2\text{NO}_2\text{ClO}_4$	NENP	46.2–48	10–16	13–7	2.1–2.2	9.8–13.4	[40,41]
$\text{Ni}(\text{C}_3\text{H}_{10}\text{N}_2)_2\text{NO}_2\text{ClO}_4$	NINO	50–52	11.5–16	10–15	2.2	8.9–11.2	[42,43]
$\text{Ni}(\text{C}_3\text{H}_{10}\text{N}_2)_2\text{N}_3\text{ClO}_4$	NINAZ	100–145		30–44			[31,44]
Y_2BaNiO_5		250–280	50–56	60.5–110	2.16		[45,46]

^aThe experimentally measured critical field is 2.2 T in DTN, smaller than the theoretical 1D results of about 3.3 T, due to the influence of interchain interactions.

critical field strength $B_c \leq 3$ T (cf. Table I) that is very suitable for magnetic refrigeration applications. Besides these two members, there are other spin-1 chain materials in the family, including NENB [15,39], NENP [40,41], and NINO [42,43] (cf. Table I), which are very common frustration-free spin-1 materials that can be described by the Hamiltonian given by Eq. (1).

Despite a little dispute about the specific value of J and Landé factor g , consensus has been reached that the compound TMNIN can be well described by a spin-1 HAFC with negligible single-ion anisotropy [30,33], through fitting the magnetic susceptibility [30], specific heat [32], and magnetization curve [31]. Below, to explore the MCE properties of materials with the corresponding theoretical model, we take the parameter set $J = 12$ K and $g = 2.25$ from Ref. [30] for TMNIN, and choose the set of parameters $J = 2.2$ K, $D = 8.9$ K, and $g = 2.26$ for DTN [35]. Before discussing the iMCE properties and performances of the spin-1 chain refrigerants, we note that TMNIN can be regarded as an excellent spin-1 HAFC material that corresponds to a gapped ground state, while the DTN has $D/J \simeq 4$ and resides well in the trivial large- D phase. TMNIN opens up the spin excitation gap due to the emergence of SPT order, in sharp distinction to gapless spin-1/2 materials such as CuP. Therefore, it is interesting to compare the iMCE of these two materials as *topological* Haldane vs trivial large- D magnetic refrigerants.

III. INVERSE MCE IN THE SPIN-1 CHAIN MATERIALS

Below we provide our main results of the magnetothermodynamics of two spin-1 chain magnets, i.e., the Haldane chain TMNIN and large- D chain DTN, and compare them to the spin-1/2 HAFC compound CuP (with parameters $J = 3.2$ K and $g = 2.33$ [48]). We show the MCE characteristics, including the adiabatic temperature change ΔT_{ad} , isothermal entropy change ΔS , Güneisen parameter Γ_B , and differential characterization Θ_T , etc. The practical cooling performance such as the efficiency factor η and hold time are also discussed and compared in this section.

A. Entropy curves and isothermal entropy change ΔS

Magnetic fields can tune the spin states of the system and induce significant entropy change that can then be transferred into cooling effects. In Fig. 1, we show the entropy curves at two magnetic fields—the initial field B_i and the final field B_f . As we are considering the iMCE process, they are set as $B_i = 0$, $B_f = 3.26$ T (TMNIN) and $B_i = 0$, $B_f = 3.3$ T (DTN) for the two spin-1 compounds. It should be noted that in the iMCE process, the largest required field (here B_f) is to the right of the critical field value (B_c). This is in sharp contrast to the MCE process of spin-1/2 material CuP, where $B_f = 4.09$ T (also at the QCP) and the largest field in the cooling procedure is instead $B_i = 7.14$ T, much greater than that required in the compounds TMNIN and DTN. Such significant reduction of the maximal magnetic fields is important for the implementation of the quantum magnetic refrigeration in, say, the space applications.

From the thermal entropy curves in Fig. 1, we find that the Haldane magnet TMNIN has a rather small isothermal

entropy change ΔS , clearly less than $1 \text{ J mol}^{-1} \text{ K}^{-1}$ regardless of the working temperature (cf. Fig. 2). However, the large- D magnet DTN is found to conduct a quite prominent entropy change, as seen in Figs. 1 and 2, comparable to that of the spin-1/2 compound CuP. As DTN only requires a maximal field ($B_{\max} = B_f = 3.3$ T), half of that for CuP, we find DTN has the highest “efficiency,” i.e., entropy change per Tesla, over the other two compounds, as shown in Fig. 2(b).

B. Isentropes and adiabatic temperature change ΔT_{ad}

In the iMCE cooling procedure, the compounds are first magnetized along the isothermal line AB (red arrowed line in Fig. 1). A larger ΔS means the greater cooling capacity, which, in the adiabatic process (indicated by the horizontal line BC), is translated into a large temperature change, ΔT_{ad} . When the magnet reaches its lowest temperature T_f at the point C, we contact the refrigerant with the heat load and it starts to absorb heat from there. The temperature of the magnetic refrigerant gradually rises up along the isofield line CA with a fixed field B_f .

On this basis, it becomes very meaningful to compute the isentropes of the three compounds and determine the adiabatic temperature change ΔT_{ad} from there. In Figs. 3(a) and 3(b), we show isentropes of TMNIN and DTN, where the criticality-enhanced iMCE can be clearly observed. When the magnetic field increases from zero ($B_i = 0$) to critical field ($B_f \geq B_c \simeq 3$ T for both spin-1 compounds), we find that the temperature decreases monotonically, e.g., from about 2 K to about 1 K (for TMNIN) and 500 mK (DTN). The ΔT_{ad} results are collected and shown in Fig. 4, which are found to be significant in the course of increasing fields for both TMNIN and DTN, in a wide range of initial temperatures T_i , shown up to 2.5 K.

In the isentropes of DTN (and also TMNIN) in Fig. 3, we can recognize two dips in low- T isentropic lines, which correspond to the two field-driven QCP. The lower-field one (at about 3.3 T for DTN) has strong iMCE occurring due to the closure of the spin gap, while the one at the higher field (about 11.7 T for DTN) is the saturation transition where the spins become polarized. Different from the spin-1 chains, the results of spin-1/2 CuP in Fig. 3(c) show only one saturation QCP at a field of about $B_c \simeq 4$ T. If we increase the fields from zero to B_c , the iMCE in CuP is apparently weak, while the MCE in CuP is significant when decreasing from a large B_i higher than 7 T [cf. Figs. 3(c) and 4(a)]. Therefore, to make a fair comparison, we compute the temperature change ΔT_{ad} per Tesla, i.e., $\Delta T_{ad}/B_{\max}$, in Fig. 4(b). From the same (high) initial temperatures $T_i \lesssim 2.5$ K, we find that the DTN actually has the largest ratio, and TMNIN is also more efficient than CuP.

C. Güneisen parameter Γ_B and differential iMCE Θ_T

Above we have computed the isothermal entropy change ΔS and adiabatic temperature change ΔT_{ad} of two spin-1 materials and find that the absolute and per-Tesla values are both important for characterizing iMCE properties. As a matter of fact, to compare the MCE properties more faithfully by getting rid of the influences of different field ranges, we

FIG. 3. Simulated isentropic contour plots of three spin-chain compounds, including the spin-1 materials (a) TMNIN and (b) DTN, and (c) the spin-1/2 chain CuP. There are two QCPs at lower (B_c) and upper (B_s) critical fields in (a) and (b), where $B_c = 3.26$ T (and $B_s \simeq 32$ T, not shown) [49] for TMNIN and $B_c = 3.3$ T, $B_s = 11.7$ T for DTN. Between B_c and B_s , there exists a continuous Tomonaga-Luttinger liquid (TLL) regime with relatively flat isentropic lines at low temperature.

exploit the differential characterizations including the Grüneisen parameter Γ_B and differential entropy change Θ_T . With these, we are able to compare the MCE properties point by point at each magnetic field.

The Grüneisen ratios Γ_B of three spin-chain materials are compared in Fig. 5. In all three cases, we find pronounced peaks in Γ_B that change its sign abruptly near the QCP [11,12], revealing the quantum criticality-enhanced MCE. The height of the Γ peak represents the adiabatic temperature change rate under an infinitesimal field change, which increases as T lowers and diverges as $T \rightarrow 0$ [11]. Again, we see that the Γ_B peaks of TMNIN are much weaker than those of DTN and CuP at the same temperature. The positive peaks and negative dips represent, respectively, the MCE and iMCE in the materials, which are quite different for the spin-1 DTN and spin-1/2 CuP materials. For DTN, Γ_B is negative (iMCE) in the small-field side and positive (MCE) on the other, with the negative dip much more pronounced as compared to the positive peak, i.e., the iMCE in DTN is much stronger than MCE. On the contrary, CuP exhibits exactly the reverse behaviors, i.e., with a pronounced MCE peak to the right of the critical field, while a very weak iMCE peak on the left. This can be understood as the TLL phase appears at different sides of the QCP in the two compounds CuP and DTN.

FIG. 4. (a) The adiabatic temperature change ΔT_{ad} and (b) temperature change per Tesla, $\Delta T_{ad}/B_{max}$, of the three spin-chain compounds considered in this work.

The results of the entropy change rate Θ_T are shown in Fig. 6, which presents the clear positive peaks (iMCE) and negative dip (MCE) around the critical fields at low temperature. Similar to the observations in Γ_B , TMNIN again have only rather weak peaks (dips) in Θ_T , while DTN has a pronounced peak with a height of a similar magnitude to the dip in the CuP curve [Fig. 6(c)], showing strong iMCE. Both Γ_B and Θ_T display characteristic divergent behaviors close to the QCP and change signs as the field crosses the critical point, indicating the pronounced refrigeration effects through adiabatic demagnetization (MCE) and magnetization (iMCE).

D. iMCE performance: Efficiency factor η and hold time

In practical applications, the refrigeration efficiency factor η and the hold time are of significance to maintain a sustainable and high-efficiency refrigeration procedure. The efficiency factor η is the ratio between heat absorbed Q_c from the heat load (i.e., the area of the dashed line between the AC and DE lines in Fig. 1) and the released heat Q_m to the heat reservoir, i.e., $\eta = Q_c/Q_m$. For DTN, the area of the red shadow in Fig. 1 is $\Delta Q_c = 0.915$ J/mol, similar to that of the spin-1/2 material CuP with $\Delta Q_c = 1.144$ J/mol, while requiring less than half the field. For the Haldane refrigerant TMNIN, we see a small heat absorption $\Delta Q_c = 0.227$ J/mol, again outperformed by the large- D magnet DTN. Besides the heat absorption, we are also interested in the heat release Q_m in the isothermal process (area of the rectangle ABDE), as there heat has to be expelled to the outer environment and thus constitutes a load for, e.g., mechanical cooling or higher-stage ADR. For a robust and efficient refrigeration system, we want the refrigerant to absorb Q_c as large as possible while, at the same time, releasing a smaller amount of heat to the environment, i.e., to have a high efficiency factor η [7,8]. From Fig. 1, we find that such a rate of the compound DTN is $\eta = 47.5\%$ when working between $T_i = 1.3$ and $T_f = 0.09$ K, which is considerably higher than that of CuP (26% from the same initial temperature T_i as reported in Refs. [16,17]).

After the adiabatic demagnetization process (BC line in Fig. 1), the refrigerant temperature reaches the lowest value T_f at the magnetic field $B_f = B_c$. After that, the refrigerant contacts with the load and its temperature rises along the isofield line CA. We want the refrigerant with good performance to absorb heat without warming up too rapidly. The simulated

FIG. 5. The simulated Grüneisen parameter Γ_B of three materials: (a) DTN, (b) CuP, and (c) TMNIN, shown at various temperatures from 1000 mK down to 200 mK. The red vertical dashed line indicates the critical magnetic fields of the three spin-chain materials.

temperature T_S at time t is

$$T_S(t) = T_S(0) + \dot{Q}/C_m,$$

which mainly depends on the magnetic specific heat C_m of the refrigerant and heat load $\dot{Q}$. We assume that the heat is transferred at a constant rate $\dot{Q} = 5 \mu W$ typical for space applications [16], and start from an initial temperature $T_S(0) = 0.01 J/k_B$, where J is the spin coupling constants of the compound. The results, i.e., temperature $T_S(t) - T_S(0)$ versus time t , of the three compounds are shown in Fig. 7, from which we find that the spin-1 DTN has a very similar hold time as that of the spin-1/2 CuP. The hold time of the latter has been shown to be quite competitive as compared to commonly used paramagnetic salts [16]. Overall, we find that the spin-1 magnetic refrigerant DTN provides excellent MCE performance in terms of efficiency factor η and hold time.

IV. DISCUSSION AND OUTLOOK

Clearly distinct from the paramagnetic ADR where only isolated ions are involved in the demagnetization cooling process, here in quantum magnetic refrigeration we exploit the correlation and entanglement of the spins and the strong quantum fluctuations as our resource of cooling capacity, and significant temperature decrease can be gained in both demagnetization (MCE) and magnetization (iMCE) processes. Moreover, different from the conventional (classical) MCE that is most prominent near thermal Curie phase transition at finite temperature, quantum refrigeration is strongly enhanced near the quantum phase transitions at $T = 0$. The strongly fluctuating thermal states near the quantum critical point prevent the constituents, i.e., spins, from freezing at low temperatures and even until zero temperatures, resulting in

FIG. 6. The simulated entropy change rate Θ_T of three materials: (a) DTN, (b) CuP, and (c) TMNIN, shown at various temperatures, from 360 down to 120 mK.

FIG. 7. The sample temperature T_s as a function of time t at a fixed field $B = B_f$, calculated under a constant heat load of $5 \mu\text{W}$. We consider a 100 g substance of the spin-1/2 CuP (blue dashed line), TMNIN (gray dashed line), and DTN (orange solid line) in the calculations.

large entropy change and divergent differential refrigeration characteristics Γ_B and Θ_T , etc., as T goes to zero.

Here we have systematically investigated the iMCE near the field-induced quantum critical point in the spin-1 quantum magnets. As these compounds have a finite spin gap either due to the Haldane topological origin (in TMNIN) or large single-ion effects (DTN), significant iMCEs have been observed when the spin gap is closed. In particular, the latter is found to have comparable cooling capacities and even better performance as compared to the criticality-enhanced MCE material CuP, with considerably reduced magnetic fields required.

Moreover, in the compound DTN, the field-induced quantum phase transition can be described as a Bose-Einstein condensation in quantum magnets, and has a high thermal conductivity even at very low temperature [23]. As the typical paramagnetic salts have low thermal conductivity since the spins do not talk to each other in the “gas” states, here in the spin-1 compounds heat can be transferred through the magnetic excitations between the coupled spins. This renders the spin-1 magnet DTN as a very promising quantum magnetic refrigerant with both high cooling capacities and excellent performance.

The compounds DTN and TMNIN are very classic spin-1 chain materials and their single-crystal samples have been synthesized for quite some time. For example, a high-quality single crystal of DTN has been used in the studies of Bose-Einstein condensation in quantum magnets [34,35] and thermal transport measurements [23,37]. Therefore, above we only consider the iMCE in single-crystal DTN samples, and the fields are applied along the single-ion c axis. In the case that only powder samples are available or when the field tilts at an angle with respect to the single-crystal c axis, we need to consider the iMCE properties of DTN under a tilted field. We have also performed the calculations and found that the

FIG. 8. (a) Low-temperature magnetization curves under magnetic fields along various directions, including the c axis (longitudinal field B_z), tilted directions $B_x/B_z = 0.1, 0.5$, and the transverse field (B_x). (b) The derivative dm/dB of the three cases.

field-induced QCP as well as enhanced iMCE are still present for a range of tilting angles (see Appendix B).

Lastly, normal and inverse MCE properties for magnets with high Curie temperatures have been intensively discussed for room- or near-room-temperature refrigeration [50–54], which helps one to enhance the cooling capacity and design compact continuous refrigeration machinery [55]. Similarly, the efficient iMCE refrigerant, e.g., spin-1 DTN here, is important for designing a low- T continuous cooling cycle where the temperature can be decreased in both the magnetization and demagnetization processes. Our work fills this gap by finding DTN to be a very promising iMCE compound that provides a high-performance refrigerants in the “arsenal” of spin-chain quantum materials.

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APPENDIX A: LINEARIZED TENSOR RENORMALIZATION GROUP METHOD

The thermodynamics of the spin-chain models and materials can be calculated via the thermal-state tensor

FIG. 9. (a),(b) The simulated isentropic contours and (c),(d) the Grüneisen parameters under tilted fields ($B_x/B_z = 0.1$ and 0.5). The lower critical fields are slightly modified in the two cases, and the Γ_B dip characterizing iMCE becomes less pronounced for $B_x = 0.5 B_z$ as compared to that of $B_x = 0.1 B_z$.

renormalization group (TRG) methods. In this work, we employ the linearized TRG (LTRG) [21,22] proposed by some of the authors to perform the finite- T simulations. For the spin-1 chain model given by Eq. (1), the Hamiltonian can be divided into odd and even parts through the Trotter-Suzuki decomposition [56], and the thermal density matrix can be expressed as

$$\hat{\rho}_\beta = e^{-\beta H} = (e^{-\tau H})^n \simeq (e^{-\tau H_{\text{odd}}} e^{-\tau H_{\text{even}}})^n, \quad (\text{A1})$$

where n is a sufficiently large integer and the (small) imaginary time slice is $\tau = \beta/n$. In practice, τ is chosen as 0.05 and we iteratively project the imaginary evolution gates $e^{-\tau H}$ of a single Trotter step to the matrix-product density operator, so

as to cool down the temperature. In the bilayer algorithm, the density matrix at an inverse temperature β is obtained by

$$\hat{\rho}_\beta = \hat{\rho}_{\beta/2}^\dagger \cdot \hat{\rho}_{\beta/2}, \quad (\text{A2})$$

which saves the cost of calculations (by half) and considerably improves the accuracy by assuring positivity of the density matrix [22].

APPENDIX B: QUANTUM PHASE TRANSITION AND MAGNETOCALORIC EFFECTS UNDER TILTED FIELDS

When only powder samples are available or a small misalignment of the field direction occurs for a single-crystal sample, the iMCE properties of DTN need to be reconsidered as the fields can be applied along directions other than the single-ion c axis. In Fig. 8, we show the low- T magnetization process along the tilted directions as described by the Hamiltonian

$$\mathcal{H} = \sum_i J \vec{S}_i \cdot \vec{S}_{i+1} + D(S_i^z)^2 + g\mu_B(B_x S_i^x + B_z S_i^z),$$

with the total field strength $B = \sqrt{B_x^2 + B_z^2}$. In Fig. 8, we computed the cases $B_x = 0.1 B_z$ ($\theta = 5.71^\circ$) and $B_x = 0.5 B_z$ ($\theta = 26.6^\circ$), and find there still exists criticality-enhanced iMCE when tilting the longitudinal field from the c axis with an angle θ . Correspondingly, in Fig. 9 we clearly see the iMCE near the field-induced QCPs, including the evident temperature decrease and clear dip in the Grüneisen parameter Γ_B .

On the other hand, when the field is applied perpendicular to the single-ion axis (i.e., B_x with $\theta = 90^\circ$), indeed we observe that the QCP is absent (Fig. 8) and thus no pronounced iMCE can be observed. Based upon these calculations, we find that the quantum criticality enhanced iMCE exists for certain tilted fields, but not for too large tilting angles (e.g., a perpendicular B_x). Nevertheless, when the tilting angle is small (e.g., $\theta = 5.71^\circ$), we find the iMCE rather robust and barely changed as compared to that along the c axis.

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