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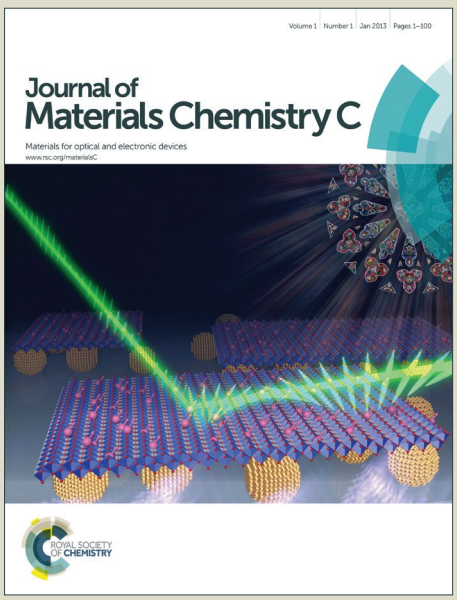

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ARTICLE

A Brilliant Cryogenic Magnetic Coolant. Magnetic and Magnetocaloric Study of the Ferromagnetically Coupled GdF_3†

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The use of paramagnetic molecules as cryogenic coolants usually requires relatively large fields to obtain a practical cooling effect. Thus, research for magnetic molecular materials with larger MCEs in fields of ≤ 2 T is the central science. In this work, the crystal structure, magnetic susceptibility and isothermal magnetization for inorganic framework material GdF_3 were measured, and the isothermal entropy change was evaluated up to 9 T. Thanks to combination of the large isotropic spin of Gd^{3+}, the dense structure and the weak ferromagnetic interaction, an extremely large $-\Delta S_m$ for GdF_3 was observed up to 528 mJ cm^{-3} K^{-1} for $\Delta\mu_0 H = 9$ T, proving itself to be an exceptional cryogenic magnetic coolant.

Introduction

The magnetocaloric effect (MCE) was discovered in 1881 in metallic iron by Warburg,[1] and the magnetic refrigeration soon become a powerful technique to obtain and maintain ultra-low temperature by adiabatic demagnetization (ADR).[2-3] At an early stage, the cryogenic magnetic coolants are mainly the inorganic paramagnetic salts and oxides, such as $Gd_2(SO_4)_3{\cdot}8H_2O$ and $Gd_3Ga_5O_{12}$ (GGG).[4] In recent years, molecular materials suddenly emerged in this field as an unprecedented classification, and a lot of highly competitive molecular magnetic coolants of 3d,[5-11] 3d-4f[12-21] and 4f-types[22-29] have been synthesized and characterized. Their distinct advantages, such as stoichiometric composition, monodispersity and modifiability, have provided the researchers a perfect platform to realize the design strategies towards cryogenic magnetic coolants. Various lessons have been learned and proved, including but not limited to the large spin state, low anisotropy, weak interaction and large metal-to-ligand ratio.[30-35]

For the best cooling performance around liquid helium temperature, it is believed that the Gd^{3+} ion is a wonderful choice owing to the half-filled 4f orbital (S = 7/2), magnetic isotropy and usually weak exchange interactions. Additionally, the low magnetic ordering temperature can still be maintained even with high metal-to-ligand ratio, and a large MCE can be obtained, especially with volumetric units.[36-37] Soon after, the competition in molecular magnetic coolants became the race on the reduction of counterions accompanying Gd^{3+}. To date, many gadolinium carboxylates including acetates, formats and oxalates have been reported, with increasing MCE chasing after GGG.[38-42]

Since there is little room for the organic ligands to keep shrinking, the most recent focus in this field dramatically returned to the inorganic compounds based on small counterions such as OH^-, SO_4^{2-}, O^{2-}.[43-45] Following the strategies learned in molecular systems,[30-35] significant enhancement of MCE in these inorganic compounds have been observed, and the orthorhombic $Gd(OH)CO_3$ finally surpass the performance of GGG and set a new record.[46] However, the story seems not over yet as a better example of $GdPO_4$ was reported just after half a year.[47]

In the inorganic area, the utilization of the aforementioned strategies must be more careful, because strong magnetic interactions are more likely to exist, thus hinder the MCE. Compared with relatively versatile magnetic interaction transmitted by the OH^-, SO_4^{2-}, O^{2-} bridges, weak ferromagnetic coupling transmitted by bent μ-F^- bridges is often observed in lanthanide complexes,[48-49] which urge us to investigate the MCE performance of gadolinium fluoride. Although GdF_3 was tested as the working material for a toroidal ADR prototype,[50] the presence of Gd_2O_3 impurity prevented the intrinsical magnetocaloric performance of GdF_3 from unrevealing. Herein we report the detailed magnetic and magnetocaloric study on the pure sample of GdF_3. The occurrence of ferromagnetic coupling and extremely large MCE proves it to be the best cryogenic magnetic coolant ever reported.

Experimental section

Synthesis of GdF_3

Pure polycrystalline GdF_3 can be hydrothermally synthesized using analytical reagent (> 99.9%) of aqueous $GdCl_3$ and excess amount of $NaBF_4$ or NH_4F, while commercial product is also available.

X-ray Crystallography

The X-ray powder diffraction data for structure refinement was collected on Bruker D8 Advance with Cu K_α X-ray radiation (40 kV, 40 mA). The step-scanned X-ray powder diffraction data was recorded in the 2θ range of 20-115° with 0.02° 2θ step and 8 seconds/step scan speed. The structural model of TbF_3 (in space group *Pnma*) was used as the initial structural models for Rietveld refinement, which was carried on Reflex Powder Refinement module of Material Studio. The structural parameters, together with Pseudo-Voigt profile parameters, background parameters, the cell constants, the zero point of the diffraction pattern, the Berar-Baldinozzi asymmetry correction parameters and the March-Dollase preferred orientation correction parameters, were optimized step by step to improve the agreement between the calculated and the experimental powder diffraction pattern. The final Rietveld refinement plot is shown in Fig. S1. Further details on the crystal structure may be obtained in the ESI (Tables S1 and S2) and from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), by quoting the depository number CSD-429920 (GdF_3).

Physical Measurements

Magnetic measurements were performed on polycrystalline sample of GdF_3 using a Quantum Design PPMS with VSM option. Variable-temperature magnetic susceptibility measurement was performed on polycrystalline sample in an applied dc field of 0.1 T between 2 ~ 300 K, and the isothermal magnetization were measured from 2 K to 10 K in an applied dc field up to 9 T. Diamagnetic correction was applied based on the Pascal's constant. Low-temperature specific heat was studied on a Quantum Design PPMS up to 9 T with the ^{3}He option adopting standard relaxation technique.

Table 1 Crystal Data and Structural Refinement for GdF_3.

Chemical formula	GdF_3
Formula Mass / g mol^{-1}	214.25
Crystal system	Orthorhombic
Space group	*Pnma*
Z	4
a/Å	6.5718(1)
b/Å	6.9844(1)
c/Å	4.3903(1)
Unit cell volume/Å^3	201.21
ρ_{calcd} / g cm^{-3}	7.062
R_p	1.62%
R_{wp}	2.21%

Results and discussion

Crystal Structure

Although the powder X-ray diffraction pattern of GdF_3 was listed in JCPDF #49-1804, the exact crystal structure has not been determined. Here by the Rietveld refinement on the Powder X-ray diffraction pattern (**Figure S1**), it is found that GdF_3 crystallizes in the orthorhombic space group *Pnma* and shares the same structure for SmF_3, EuF_3, TbF_3, HoF_3 and YbF_3 (**Table 1**). In the crystal structure, each Gd^{3+} ion is 9-coordinated in a tricapped trigonal prismatic geometry (**Figure 1**), while each F^- ion is μ_3-bridging, just corresponding to the stoichiometric ratio 1:3. The lengths of Gd-F bonds are generally similar, ranging from 2.331 to 2.501 Å, while the Gd-F-Gd angles are quite different, lying between 98.88° and 139.03°. The nearest Gd···Gd separations are 3.672 Å, which form a series of zigzag chains along the *a* axis and then further extended into a 3-dimentional framework (Figure 1 and Figure S2). Thanks to the simple composition, the formula mass of GdF_3 is only 214.25 g mol^{-1}, trapping as much as 73.4% of Gd^{3+} in an extremely dense structure with ρ = 7.062 g cm^{-3}. Therefore, GdF_3 shall be a wonderful magnetic coolant so long as there isn't long-range antiferromagnetic ordering in the working temperature region.

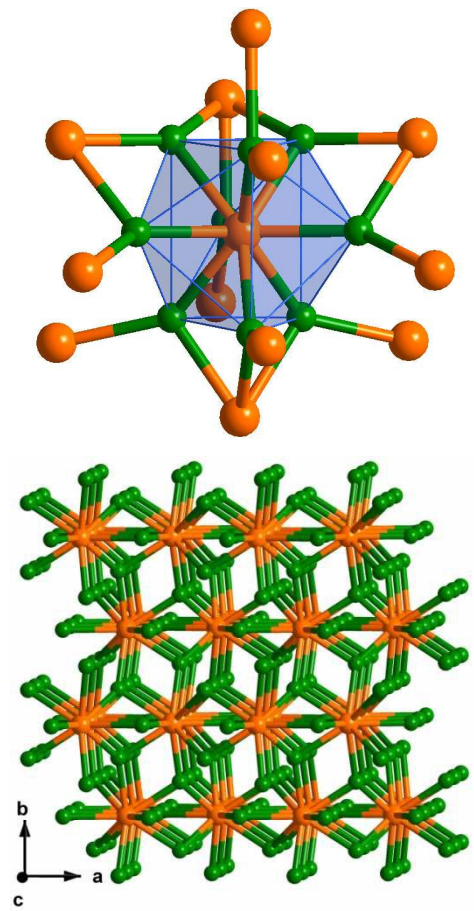

Figure 1 The crystal structure of GdF_3. Top: The coordination environment of Gd^{3+}; Down: The extended framework of GdF_3 viewed along the *c* axis. Colour Codes: Gd, orange; F, green.

Magnetic Properties

Variable-temperature magnetic susceptibility measurement was performed on polycrystalline sample of GdF_3 in an applied dc field of 0.1 T (**Figure 2**). At room temperature, the $\chi_m T$ value is 7.96 cm^3 K mol^{-1}, slightly larger than the spin-only value expected for a free Gd^{3+} ion with g = 2 (7.875 cm^3 K mol^{-1}). Upon cooling, $\chi_m T$ keeps increasing to 11.2 cm^3 K mol^{-1} at 2 K, suggesting dominant ferromagnetic interactions between Gd^{3+} ions. The inverse magnetic susceptibility ($1/\chi_m$) obeys the Curie-Weiss law with C = 7.91 cm^3 K mol^{-1} and θ = +0.7 K. No sign of the long-range magnetic ordering can be observed above

2 K, as the ordering temperature is reported to be around 1.25 K.[51] Such a behaviour is extremely favourable for a large cryogenic MCE, and it is quite different from those complexes with hydroxide bridges, where strong antiferromagnetic interactions are common and usually harm the full utilization of the MCE. The ferromagnetic coupling in GdF_3 and the low ordering temperature rule out our last worry about its capability as a promising cryogenic magnetic coolant.

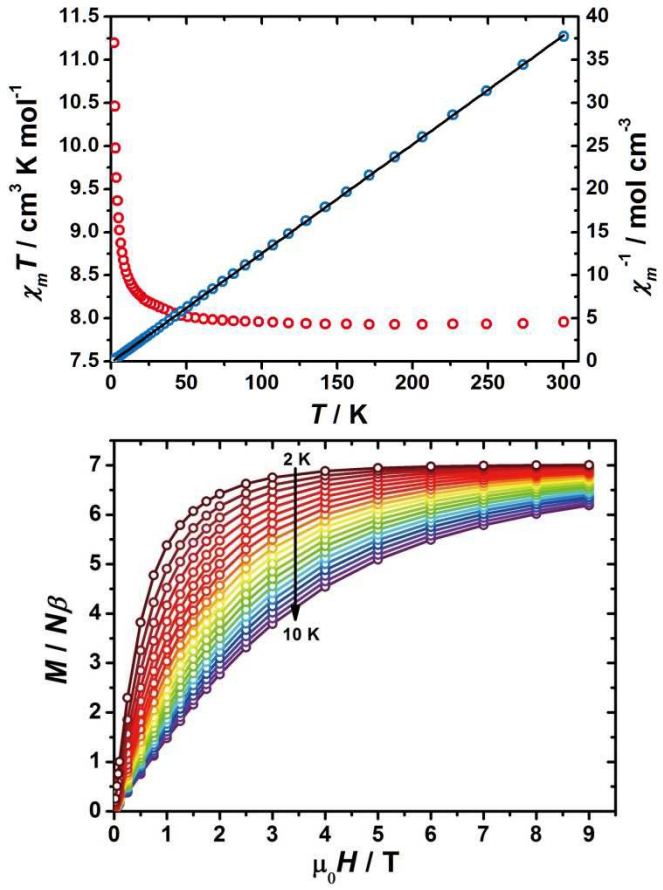

Figure 2 Magnetic Properties of GdF_3. Left: Temperature-dependencies of the magnetic susceptibility product ($\chi_m T$) and inverse magnetic susceptibility ($1/\chi_m$) at 2-300 K with a dc field of 0.1 T. Right: Magnetization *versus* the dc field in the temperature range of 2-10 K. The black solid line represents the least-square fit for the Curie-Weiss law.

To calculate the precise value of $-\Delta S_m$, the isothermal magnetization for GdF_3 were measured from 2 K to 10 K in an applied dc field up to 9 T (**Figure 2**). The magnetization increases quickly with the applied field below 2 T and reaches the saturation value of 7.0 $N\beta$ at 2 K and 9 T, which is in good agreement with the expected value for a Gd^{3+} ion ($s = {}^7/_2$, $g = 2$).

The isothermal entropy change can be calculated by applying the Maxwell equation:

$$\Delta S_m(T) = \int_0^H \left[\partial M(T, H)/\partial T\right]_H dH$$

Just as many reported ferromagnetic coupling systems, the maximum $-\Delta S_m$ values for GdF_3 grow rapidly with increasing ΔH, namely 181 mJ cm^{-3} K^{-1}, 321 mJ cm^{-3} K^{-1} and 399 mJ cm^{-3} K^{-1} for $\Delta\mu_0 H$ = 1 T, 2 T and 3 T, respectively (**Figure 3**). For larger ΔH, the increase of $-\Delta S_m$ values become slower, reaching 474 mJ cm^{-3} K^{-1} and 506 mJ cm^{-3} K^{-1} for $\Delta\mu_0 H$ = 5 T and 7 T, and the peaks of $-\Delta S_m$ *versus T* curves gradually shift to higher temperatures. These results are in line with the heat capacity tests for the toroidal ADR prototype,[51] and the maximum value here we obtained is 528 mJ cm^{-3} K^{-1} (74.8 J kg^{-1} K^{-1}) at T = 3.2 K and $\Delta\mu_0 H$ = 9 T, close to the theoretical limiting value of 570 mJ cm^{-3} K^{-1} (80.7 J kg^{-1} K^{-1}) calculated from $R\ln(2s+1)/Mw$ with $s = {}^7/_2$ and Mw = 214.25 g mol^{-1}.

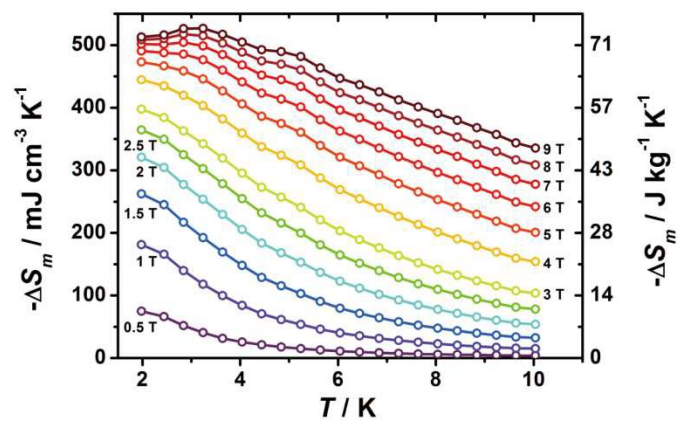

Figure 3 Temperature-dependencies of $-\Delta S_m$ for selected values of $\Delta\mu_0 H$ obtained from magnetization data. The data with field variation below 0.5 T are omitted for clarity.

Heat Capacity

The low temperature heat capacity (C) measurements were also performed to further investigate the MCE of GdF_3 (**Figure 4**), and no peak around 3.8 K corresponding to Gd_2O_3 can be found.[50] The curves shows typical trends as most cryogenic magnetic coolants, with the higher temperature region attributed to the lattice contribution and the lower part dominated by Schottky type magnetic contribution. The lattice one, C_{latt}, can be fitted to the Debye's model and yield a high Debye temperature (θ_D) of 284(3) K with r_D = 4, indicating a rigid crystal framework that is favourable to large MCE. A λ-shaped anomaly is observed in the zero field at approximately 1.21 K but suppressed by applied fields, indicating the emergence of a magnetic phase transition in good agreement with the reported 1.25 K.[51]

Then, the entropy can be obtained by numerical integration from the experimental C, using:

$$S(T) = \int_0^T C(T)/T dT$$

with a constant value base on the high temperature saturation value of magnetic entropy ($S_{m,\,sat} = R\ln(2s+1) = 2.08\ R$) added to the low-field entropy to compensate for experimental inaccessibility to absolute zero. From the heat capacity, the maximal isothermal magnetic entropy changes (ΔS_m) were obtained as 186 mJ cm^{-3} K^{-1}, 395 mJ cm^{-3} K^{-1} and 473 mJ cm^{-3} K^{-1} for $\Delta\mu_0 H$ = 1 T, 3 T and 5 T, respectively, in great agreement with the results calculated from the magnetization (**Figure 5**). These are accompanied by the large adiabatic temperature change (ΔT_{ad}) up to 17 K for $\Delta\mu_0 H$ = 5 T (**Figure**

S3), highlighting the competiveness of GdF_3 as a brilliant cryogenic magnetic coolant.

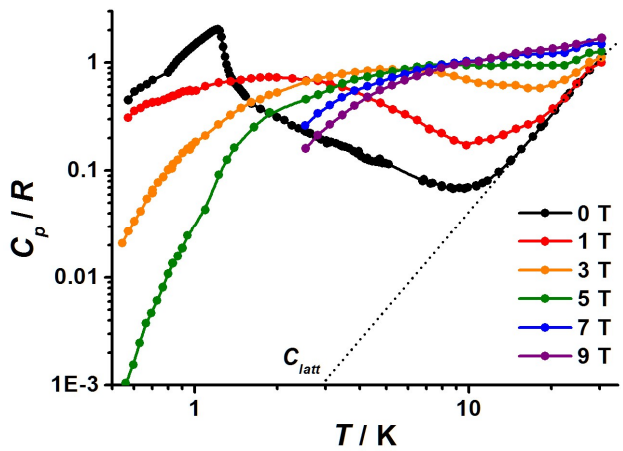

Figure 4 Temperature-dependencies of the heat capacity normalized to the gas constant in selected applied fields. The dotted line represents the lattice contribution.

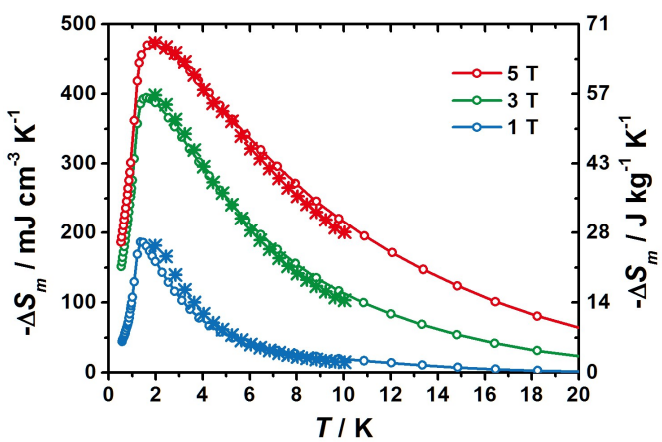

Figure 5 Temperature-dependencies of $-\Delta S_m$ obtained from magnetization (★) and heat capacity (●) for selected $\Delta\mu_0 H$.

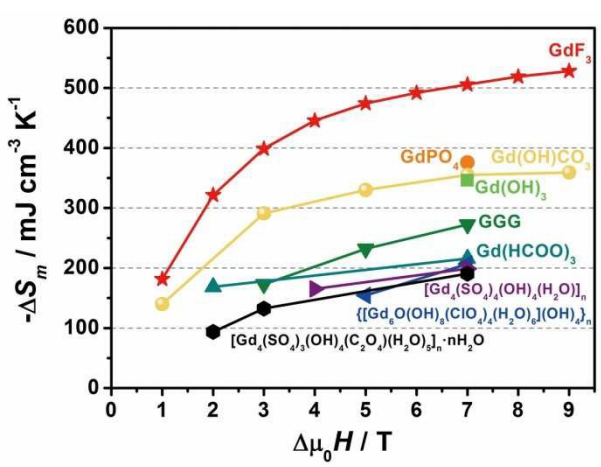

Figure 6 The maximum reported $-\Delta S_m$ value *versus* the corresponding $\Delta\mu_0 H$ for selected cryogenic magnetic coolants.

Conclusions

The area of cryogenic magnetic coolants is full of competitions, and there has never been a candidate that can hold the record for a long time. Thanks to such competition in a sense, researchers are now much wiser at adopting suitable strategies for the design of high performance magnetic coolants. Although the record set by $Gd(OH)CO_3$[46] has been taken recently, we haven't stopped seeking and finally present the ferromagnetically coupled GdF_3.

As demonstrated in **Figure 6** and **Table 2**, the other cryogenic magnetic coolant with $-\Delta S_m$ larger than 400 mJ cm^{-3} K^{-1} has never been reported, while the maximum value for GdF_3 has already exceeded 500 mJ cm^{-3} K^{-1}. Comparing the $-\Delta S_m$ with $\Delta\mu_0 H = 7$ T for the sake of fairness, the performance of GdF_3 (506 mJ cm^{-3} K^{-1}) surpass that of $GdPO_4$ (375.8 mJ cm^{-3} K^{-1})[47] by 34.6%, setting a new record. Last but not least, the dense structure and ferromagnetic interaction in GdF_3 leads to still excellent performance even for lower $\Delta\mu_0 H$ such as 2 T and 1 T, highlighting the competitiveness.

Table2. Magnetic entropy change for selected molecule-based materials.

Complex[ref]	$\Delta\mu_0 H$ (T)	$-\Delta S_{m,\,max}$ (J kg^{-1} K^{-1})	$-\Delta S_{m,\,max}$ (mJ cm^{-3} K^{-1})
$[Gd_4(SO_4)_3(OH)_4(C_2O_4)(H_2O)_5]_n \cdot nH_2O$[45]	7	51.5	190
$[Gd_4(SO_4)_4(OH)_4(H_2O)]_n$[44]	7	51.3	199
$\{[Gd_6O(OH)_8(ClO_4)_4(H_2O)_6](OH)_4\}_n$[43]	7	46.6	207
$Gd(HCOO)_3$[41]	7	55.9	216
$Gd_3Ga_5O_{12}$ (GGG)[4]	7	38.4	272
$Gd(OH)_3$[52]	7	62.0	346
$Gd(OH)CO_3$[46]	7	66.4	355
$GdPO_4$[47]	7	62.0	376
GdF_3 (This work)	2	45.5	321
	5	67.1	474
	7	71.6	506

At this point, we believe the long journey in pursuit of the best cooling performance is close to the extreme. There is limited room, if any, for the further increase of the $-\Delta S_m$ value itself for Gd-based materials: some other compounds like GdOF, GdOOH, $GdBO_3$ and $Gd_2(CO_3)_3$ might worth some try, while Gd_2O_3 and $Gd(OH)_3$[52] are already known as antiferromagnets and suffer severe decrease of the full entropy. Future study on the cryogenic MCE shall turn the focus onto the other parameters such as ΔT_{ad}, cooling power and even production cost, where the Mn-based materials become strong competitors.[11] Although we have to admit that the coordination complexes with organic ligands can never be so comparative with inorganic complexes in such sense, it should not be forgotten that the ambitions of molecular materials have never been just about the value. We have witnessed how the numerous complexes seems useless can be rationally modified into good candidates for magnetic coolants, and we have been continuously learning about the magneto-structural correlations during the design and synthesis of these complexes. Furthermore, chemists' powerful skill on material engineering can still modify the behaviour of the inorganic compounds in the limitless nanomaterial and organic-inorganic

hybrid material, where the magnetic interaction, ordering temperature and low-field performance may be fine-tuned and optimized. *It is, perhaps, the end of the beginning.*

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Notes and references

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† Electronic Supplementary Information (ESI) available: Additional crystallography tables and figures of magnetic properties. See DOI: 10.1039/b000000x/

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Graphical TOC

The magnetocaloric effect of a inorganic framework material with repeating unit of GdF_3 has been experimentally studied using isothermal magnetization and heat capacity measurements. The maximum entropy change $-\Delta S_{max}$ reaches 74.8 J kg^{-1} K^{-1} or 528 mJ cm^{-3} K^{-1} for ΔH = 9 T and T = 1.8 K.