Dalton Transactions

Accepted Manuscript

ROYAL SOCIETY
OF **CHEMISTRY**

www.rsc.org/dalton

Journal Name

COMMUNICATION

$Gd_2Cu(SO_4)_2(OH)_4$: A 3*d*-4*f* Hydroxysulfate with Enhanced Cryogenic Magnetocaloric Effect

Received 00th January 20xx,
Accepted 00th January 20xx

Yingying Tang,[a, b] Wenbin Guo,[a] Suyun Zhang,[a] Ming Yang,[a] Hongping Xiang,[a] and Zhangzhen He,[*,a]

DOI: 10.1039/x0xx00000x

www.rsc.org/

A 3*d*-4*f* hydroxysulfate, $Gd_2Cu(SO_4)_2(OH)_4$, is synthesized by means of conventional hydrothermal method. Magnetic measurements confirm that the titled compound exhibits a paramagnetic behavior down to 2 K, in which an enhanced magnetocaloric effect with a maximum of $-\Delta S_m$ (45.52(1) J/Kg·K, 212.8(6) mJ·cm^{-3}·K^{-1}) is observed at ~ 4 K for ΔH = 8 T. The thermal stability of TG and FT-IR spectrum are also characterized.

Materials with magnetocaloric effect (MCE) have attracted much interest due to their potential applications for cryogenic refrigerants with energy-efficient features. MCE was found early in nickel by Weiss and Piccard in 1917[1] and then was developed greatly since William F. Giauque found paramagnetic salts $Gd_2(SO_4)_3·8H_2O$ as cryogenic refrigerant for helium that can achieve low temperature below 1 K.[2] Low-temperature MCE is usually applied for cooling agents via adiabatic demagnetisation on the basis of the magnetic entropy change under a varying magnetic field.[3] In recent years, the search for low-temperature MCE has been focused on metal clusters and polymers due to their structural diversity, including $\{Gd_6Mn_{12}\}$,[4] $\{Gd_3Fe_2\}$,[5] $\{Gd_{12}Mo_4\}$,[6] $\{Gd_{24}\}$,[7] {MnGd},[8] $[Gd_2(OAc)_3(H_2O)_{0.5}]_n$,[9] $\{Mn_{10}\}$,[10] $\{Gd_{36}Ni_{12}\}$,[11] $\{[Gd(OH)(H_2O)(abtc)_{0.5}]·H_2O\}_n$,[12] and $[Gd(OH)CO_3]_n$.[13] Although many metal clusters and polymers have found to exhibit MCE, it should be noted that most of them cannot be considered as a cryogenic refrigerant for low-temperature applications due to a low MCE.[14]

An ideal refrigerant is usually needed to meet the following requirements: (1) a large spin ground state *S* such as Gd^{3+}, Mn^{2+}, and Fe^{3+}, since the theoretical magnetic entropy equals to $R\ln(2S+1)$; (2) a negligible magnetic anisotropy such as Cu^{2+} or Ni^{2+}, which permits easy polarization of the net molecular spins in magnetic fields of weak or moderate strength; (3) high spin degeneracy, equating to weak interactions between the magnetic centers, is important for a disordered system and large entropy. Other vital demands are the high density of magnetic centers and small non-magnetic anionic groups which act passively in the physical process.[15]

To search for low-temperature refrigerant with an enhanced MCE, the homo- or heterometallic compounds with Gd^{3+} ion ($4f^7$) may always be considered, because magnetic isotropy of Gd^{3+} ion with a large spin value will make great contribution to the entropy. The weak interactions between Gd^{3+} ions caused by the efficient shielding of outer electrons on the 4*f* orbitals will also generate multiple low-lying states, improving the entropy.[16] Furthermore, heterometallic compounds (e.g. Gd-Cu or Gd-Mn) are more advantageous to guarantee non-zero spin ground states due to their different d^n/f^n electronic configurations. To achieve high density of magnetic centers, light and short bridging groups, such as CO_3^{2-}, NO_3^-, OH^- groups, are prior to take into consideration in this regard. For example, formate ion can bind Gd^{3+} into a light and compact framework as a small bridging ligand, facilitating significant MCE for the weak interactions between the Gd^{3+} spin centers.[17] Recently, it has been found that nonmagnetic inorganic groups SO_4^{2-} may also produce higher density of magnetic centers than many ligands used by the coordinated polymers.[18]

Guided by above ideas, we have investigated the Gd^{3+}-Cu^{2+}-SO_4^{2-} system and successfully obtained a new 3d-4f hydroxysulfate, $Gd_2Cu(SO_4)_2(OH)_4$ (**1**). The structure of **1** shows a three-dimensional framework constructed by GdO_9 polyhedra, CuO_4 squares, and SO_4^{2-} tetrahedra. An unusually large MCE with a magnetic entropy change of $-\Delta S_m$ of 45.52(1) J/Kg·K (212.8(6) mJ·cm^{-3}·K^{-1}) is observed in the system.

Blue bulk crystals of **1** were prepared by the hydrothermal reaction of $CuSO_4·5H_2O$, Gd_2O_3, and K_2TeO_3 in water(Fig. S1†). K_2TeO_3 is not incorporated into this structure, but it plays a role of mineralizer in the process for that the yield of compound **1** is proved to be fruitless in the absence of K_2TeO_3. Single crystal X-ray analysis reveals that **1** crystallizes in the monoclinic space group of $P2_1/c$, which is isostructural to

---

[a] *State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, P. R. China. E-mail: hcz1988@hotmail.com; hezz@fjirsm.ac.cn*

[b] *University of the Chinese Academy of Sciences, Beijing, 100039, P. R. China*

† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

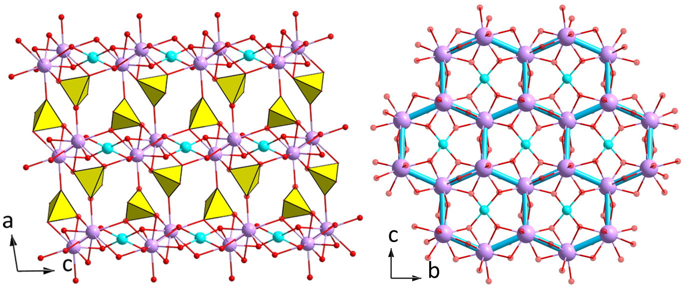

Fig. 1. View of the linkage of polyhedra for the 3D networks (left) and the 2D layers(right). Color codes: Gd, pink; Cu, blue; S, yellow; O, red. The blue dotted line shows a honeycomb lattice for Gd.

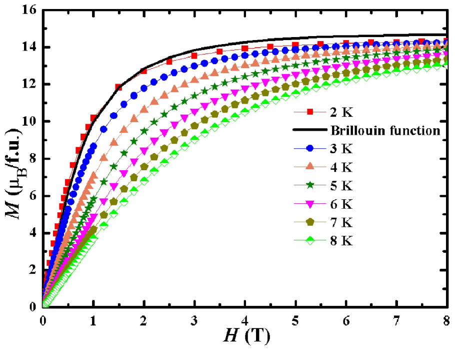

Fig. 3. The curve of magnetization versus applied field at the temperature range of 2-8 K for **1**. The black solid line represents the simulation of Brillouin function at 2 K.

$Ln_2Cu(SO_4)_2(OH)_4$ (Ln = Sm, Eu, Tb, Dy).[19] More details on crystallography data are given in Tables S1-5. The purity of the single phase was confirmed by powder X-ray diffraction studies (Fig. S2†). A complicated 3D framework (Fig. 1) is built by GdO_9 polyhedra, CuO_4 squares and SO_4 tetrahedra, in which GdO_9 polyhedra and CuO_4 squares form a two-dimensional layer and the layers are separated by SO_4 tetrahedra along the *a*-axis (also see Fig. S3†). It is noted that the layers are constructed by face- or edge-sharing GdO_9 polyhedra, showing a honeycomb-like network on the *b*-*c* plane, in which all of CuO_4 squares are located at the centers of GdO_9-channels. The neighboring Gd···Gd separations in the layer are about 3.74(6) and 4.16(9) Å. The CuO_4 squares connect to GdO_9 polyhedra with the shortest Cu-Gd distances of 3.40(4), 3.90(7) and 3.98(5) Å, while the Cu-Cu distances between isolated CuO_4 squares are 6.34(7) and 6.70(2) Å. The shortest distance between layers is 6.34(2) Å.

Figure 2 shows the dc magnetic susceptibility (χ) and corresponding reciprocal one (χ^{-1}) of **1** measured at an applied field of 0.1 T. The susceptibility increases with decreasing temperature and no any anomalies can be observed down to 2 K, indicating a paramagnetic behavior at low temperature. Magnetic susceptibility between 2-300 K follows well the Curie-Weiss law, giving the Curie constant C = 16.04(9) $emu\cdot mol^{-1}\cdot K$ and the Weiss temperature $\Theta = -0.44(8)$ K. The effective magnetic moment can be calculated to be 6.5(4) μ_B based on the equation of $\mu_{eff}^2 = 8C$, which is in good agreement with the theoretical value of 6.55 μ_B for 1/3 Cu^{2+} (S = 1/2, g = 2) and 2/3 Gd^{3+} (S = 7/2, g_J = 2).[20] The small negative Weiss temperature shows that magnetic ions Cu^{2+} ions or Gd^{3+} ions are coupled with weak antiferromagnetic interaction exchanges.

To identify the paramagnetic behavior, the isothermal magnetization as a function of applied field (*M*-*H*) was measured at 2-8 K (Fig. 3). The magnetization increases with field at 2 K and saturates at high field. The saturated magnetization value of 14 μ_B is obtained, which is close to the theoretical one of 15 μ_B. The reduction of the magnetization may be due to small amount of nonmagnetic impurities or the net antiferromagnetism between magnetic ions.[4] Also, the magnetization curve is well fitted by the Brillouin function[21], confirming the paramagnetic behavior corresponded to almost isolated magnetic ions. Moreover, the *M*-*H/T* curves at different temperatures are superposed together, confirming the negligible anisotropy in this system (Fig. S4†).[18,22]

To further confirm MCE of **1**, the change of entropy ($-\Delta S_m$) is calculated by the Maxwell relation $\Delta S_m(T)\Delta H = \int [\partial M(T,H)/\partial T]_H dH$.[23] Fig. 4 shows the temperature dependence of $-\Delta S_m$ measured at different fields. It is noted that the maximum of $-\Delta S_m$ shifts to higher temperature with increasing magnetic fields and reaches a peak with the value of 45.52(1) $J/Kg\cdot K$ (212.8(6) $mJ\cdot cm^{-3}\cdot K^{-1}$) at ~ 4 K for ΔH = 8 T. It is well-known that the magnetic entropy can be assumed as 63.20(7) $J/Kg\cdot K$ by the equation of $2R\ln(2S_{Gd}+1) + R\ln(2S_{Cu}+1)$ [4,24,25], if

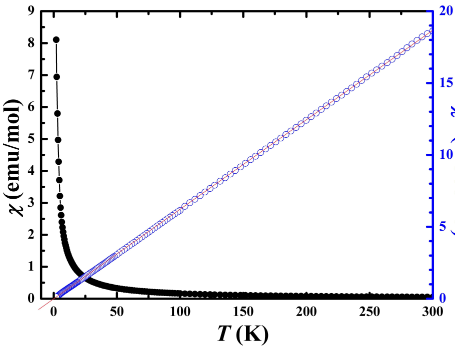

Fig. 2. Temperature dependence of magnetic susceptibility and corresponding reciprocal one for **1**. The red solid line is the best-fitted simulation of Curie-Weiss law.

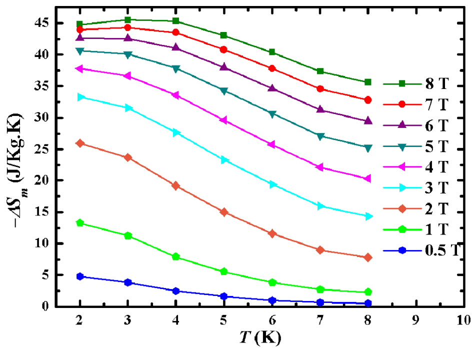

Fig. 4. View of the $-\Delta S_m$ using the magnetic data for **1** at various fields of 0.5-8 T and temperatures of 2-8 K.

the magnetic Cu^{2+} and Gd^{3+} ions are completely decoupled. The difference between the experimental and theoretical magnetic entropy suggests that weak magnetic exchanges may appear between Cu^{2+} and Gd^{3+} ions of this system, reducing the maximum entropy.

For technical applications of a cryogenic refrigerant, the magnetic entropy per volume is suggested to be more important than per mass[24]. The magnetic entropy per volume (212.86 $mJ \cdot cm^{-3} \cdot K^{-1}$) of **1** is quite large for ΔH = 8 T at 4 K. Such enhanced MCE of **1** may be due to the large mass density, ρ = 4.676 $g \cdot cm^{-3}$, corresponding to small inorganic groups of SO_4^{2-}. In fact, a large MCE value under low magnetic field may be more useful than that under high magnetic field for practical applications. A large MCE value of 122.0 $mJ \cdot cm^{-3} \cdot K^{-1}$ is observed in **1** for ΔH = 2 T at 2 K, which is close to 145.0 $mJ \cdot cm^{-3} \cdot K^{-1}$ of $Gd_3Ga_5O_{12}$ (GGG) that has been used commercially as a promising magnetic refrigerant for liquid helium below 4.2 K.[14b] This means that **1** may be a potential magnetic refrigerant in low-temperature application, due to a large MCE value.

To investigate the thermal stability of **1**, the sample is heated up to 1100 °C under a nitrogen atmosphere in Fig. 5. It is noted that compound **1** exhibits two main steps of weight loss in the temperature range of 30-1100 °C. The first step appears in the temperature range of 600-728 °C, attributing to the loss of two H_2O molecules from the dehydration of OH^- groups[26-29], since the observed weight loss of 5.64% for the plateau is close to the calculated one, 5.66%. The second step is observed between 882 and 996 °C, corresponding to the release of SO_3, since the observed weight loss of 12.53% is close to the calculated one of 12.88%. The total weight loss is about 22.2% at 1100 °C. Also, the residuals at 900 °C with 6 hours were confirmed to be the mixture of $Gd_2O_2(SO_4)$ and CuO (Fig. S5†). The decomposition reaction of **1** may be according to the following equation:

$$Gd_2Cu(SO_4)_2(OH)_4 \longrightarrow Gd_2O_2(SO_4)+CuO+SO_3\uparrow+2H_2O$$

Compound **1** is also characterized by the FT-IR spectrum (Fig. S6†). Two sharp peaks at 3579 and 3441 cm^{-1} are due to the stretching modes of OH groups and another bands at around 1634, and 858 cm^{-1} are attributed to their bending modes. All of the fundamental modes (ν_1, ν_2, ν_3, and ν_4) related to SO_4^{2-} ion could also be observed clearly in the spectrum. The ν_1 and ν_2 modes, characterizing the lowering of site symmetry from T_d group, appear at 952 cm^{-1} and 453 cm^{-1}, respectively. Particularly, the typical ν_3 mode of SO_4^{2-} ion splits into three separate peaks from 1236 to 996 cm^{-1}, and the peaks between 730-600 cm^{-1} belong to the ν_4 mode.

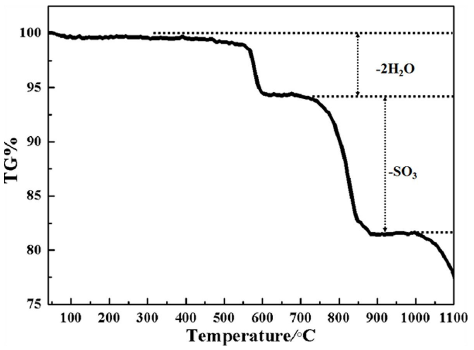

Fig. 5. Thermogravimetric curve for the decomposition of **1**.

In summary, a novel 3d-4f hydroxysulfate has been synthesized by a conventional hydrothermal method. This compound features a 3D network comprised by GdO_9 polyhedra, CuO_4 squares and SO_4^{2-} tetrahedra. Magnetic measurements indicated that **1** behaves like a paramagnet which exhibits a large MCE of $-\Delta S_m$ (45.52(1) J/Kg, 212.8(6) $mJ \cdot cm^{-3} \cdot K^{-1}$) at ~ 4 K for ΔH = 8 T. Also, this compound can be stable below 600°C. We suggest that **1** may be considered as a potential magnetic refrigerant for low-temperature application due to its enhanced MCE.

Acknowledgements

This work was financially supported by the National Basic Research Program of China (No. 2012CB921701) and National Natural Science Foundation of China (No. 21403234).

Notes and references

1 (a) P. Weiss and A. Piccard, *J. Phys.*, 1917, **7**, 103; (b) A. Smith, *Eur. Phys. J. H*, 2013, **38**, 507.
2 W. F. Giauque and D. P. MacDougall, *Phys. Rev.*, 1933, **43**, 768.
3 M. Evangelisti and E. K. Brechin, *Dalton Trans.*, 2010, **39**, 4672.
4 J.-L. Liu, W.-Q. Lin, Y.-C. Chen, J.-D. Leng, F.-S. Guo, and M.-L. Tong, *Inorg. Chem.*, 2013, **52**, 457.
5 H. Li, W. Shi, Z. Niu, J.-M. Zhou, G. Xiong, L.-L. Li, P. Cheng, *Dalton Trans.*, 2015, **44**, 468.
6 Y. Zheng, Q.-C. Zhang, L.-S. Long, R.-B. Huang, A. Müller, J. Schnack, L.-S. Zheng and Z. Zheng, *Chem. Commun.*, 2013, **49**, 36.
7 L.-X. Chang, G. Xiong, L. Wang, P. Cheng and B. Zhao, *Chem. Commun.*, 2013, **49**, 1055.
8 F.-S. Guo, Y.-C. Chen, J.-L. Liu, J.-D. Leng, Z.-S. Meng, P. Vrábel, M. Orendáč and M.-L. Tong, *Chem.Commun.*, 2012, **48**, 12219.
9 G. Lorusso, M. A. Palacios, G. S. Nichol, E. K. Brechin, O. Roubeau and M. Evangelisti, *Chem.Commun.*, 2012, **48**, 7592.
10 M. Manoli, R. D. L. Johnstone, S. Parsons, M. Murrie, M. Affronte, M. Evangelisti and E. K. Brechin, *Angew. Chem., Int. Ed.*, 2007, **46**, 4456.
11 J.-B. Peng, Q.-C. Zhang, X.-J. Kong, Y.-P. Ren, L.-S. Long, R.-B. Huang, L.-S. Zheng and Z. P. Zheng, *Angew. Chem., Int. Ed.*, 2011, **50**, 10649.
12 S. W. Zhang, E. Y. Duan and P. Cheng, *J. Mater. Chem. A*, 2015, **3**, 7157.
13 Y.-C. Chen, L. Q, Z.-S. Meng, D.-F. Yang, C. W, Z. D. Fu, Y.-Z. Zheng, J.-L. Liu, R. Tarasenko, M. Orendáč, J. Prokleška, V. Sechovsky and M.-L. Tong, *J. Mater. Chem. A*, 2014, **2**, 9851.
14 (a) B. Daudin , R. Lagnier , B. Salce, *J . Magn. Magn. Mater.*, 1982 , **27**, 315; (b) W. Dai, E. Gmelin and R. Kremer, *J. Phys. D Appl. Phys.*, 1988, **21**, 628; (c) T. Numazawa , K. Kamiya , T.

Okano , K. Matsumoto , *Physica B*, 2003, **1656**, 329; (d) A. M. Tishin and Y. I. Spichkin, *The Magnetocaloric Effect and its Application*, IOP Publishing, Bristol and Philadelphia, 2003; (e) M. Manoli, A. Collins, S. Parsons, A. Candini, M. Evangelisti and E. K. Brechin, *J. Am. Chem. Soc.*, 2008, **130**, 11129; (d) Y. Yang, Q.-C. Zhang, Y.-Y. Pan, L.-S. Long and L.-S. Zheng, *Chem. Commun.*, 2015, **51**, 7317.

15 M. Evangelisti, O. Roubeau, E. Palacios, A. Camón, T. N. Hooper, E. K. Brechin and J. J. Alonso, *Angew. Chem., Int. Ed.*, 2011, **50**, 6606.

16 M. Andruh, J.-P. Costes, C. Diaz and S. Gao, *Inorg. Chem.*, 2009, **48**, 3342.

17 G. Lorusso, J. W. Sharples, E. Palacios, O. Roubeau, E. K. Brechin, R. Sessoli, A. Rossin, F. Tuna, E. J. L. McInnes, D. Collison and M. Evangelisti, *Adv. Mater.*, 2013, **25**, 4653.

18 H.-C. Hu, C.-S. Cao, Y. Yang, P. Cheng and B. Zhao, *J. Mater. Chem. C*, 2015, **3**, 3494.

19 Y. Y. Tang, M. Y. Cui, W. B. Guo, S. Y. Zhang, M. Yang and Z. Z. He, *Cryst. Growth Des.*, 2015, **15**, 2742.

20 (a) F. E. Mabbs and D. J. Machin, *Magnetism and Transition Metal Complexes*; Chapman and Hall: London, 1973; (b) B. N. Figgis and M. A. Hitchman, *Ligand Field Theory and Its Applications*; Wiley-VCH: New York, 2000; (c) J. Lin, P. Chai, K. Diefenbach, M. Shatruk and T. E. Albrecht-Schmitt, *Chem. Mater.*, 2014, **26**, 2187.

21 C. J. Ballhausen, *Introduction to Ligand Field Theory*, McGraw-Hill, New York, 1962.

22 J.-B. Peng, Q.-C. Zhang, X.-J. Kong, Y.-Z. Zheng, Y.-P. Ren, L.-S. Long, R.-B. Huang, L.-S. Zheng and Z. P. Zheng, *J. Am. Chem. Soc.*, 2012, **134**, 3314.

23 (a) V. K. Pecharsky and K. A. Gschneidner Jr., *J. Magn. Magn. Mater.*, 1999, **200**, 44; (b) Y. I. Spichkin, A. K. Zvezdin, S. P. Gubin, A. S. Mischenko and A. M. Tishin, *J. Phys. D: Appl. Phys.*, 2001, **34**, 1162.

24 Y.-Z. Zheng, G.-J. Zhou, Z. P. Zheng and R. E. P. Winpenny, *Chem. Soc. Rev.*, 2014, **43**, 1462.

25 E. Colacio, J. Ruiz, G. Lorusso, E. K. Brechin, M. Evangelisti, *Chem. Commun.*, 2013, **49**, 3845.

26 S. H. Yang, G. B. Li, J. Ju, Z. L. Yang, F. H. Liao, Y. X. Wang, J. H. Lin. *Inorg. Chim. Acta*, 2008, **361**, 2413.

27 R. Baies, V. Caignaert, V. Pralong, B. Raveau. *Inorg. Chem.*, 2005, **44**, 2376.

28 T. Yang, Y. Zhang, M. Xiong, F. H. Liao, J. H. Lin. *Solid State Sci.*, 2008, **10**, 1886.

29 S. Vilminot, G. André, F. Bourée-Vigneron, M. Richard-Plouet, M. Kurmoo. *Inorg. Chem.*, 2007, **46**, 10079.