Anisotropic magnetic property, magnetostriction, and giant magnetocaloric effect with plateau behavior in TbMn$_2$Ge$_2$ single crystal

Shuai Huang$^{1,3,*}$, Yuming Bai$^2$, Kaiqi Wan$^1$, Changming Zhu$^{1,3}$, Dexuan Huo$^1$ & Zhaoming Tian$^2$*

The ternary RMn$_2$Ge$_2$ (R = rare earth) intermetallic compounds have attracted great attention due to their interesting magnetic behaviors and magnetotransport responses. Here, we reported our observation of anisotropic magnetic property, magnetostriction, and magnetocaloric effect (MCE) in TbMn$_2$Ge$_2$ single crystal. Below the transition temperature of Tb magnetic sublattices ($T_{TbC} \sim 95$ K), strong Ising-like magnetocrystalline anisotropy is observed with an out-of-plane ferromagnetic moments $5.98 \mu_B$/f.u. along the easy $c$ axis, which is two orders of magnitude larger than that of field along $a$ axis. Above $T_{TbC}$, a field-induced metamagnetic transition is observed from the spin-flip of Mn sublattices. During this transition, remarkable magnetostriction effect is observed, indicating of strong spin–lattice coupling. The responses of Tb and Mn sublattices to the magnetic field generate a giant magnetic entropy change ($-\Delta S_M$) and large values of relative cooling power (RCP) and temperature-averaged entropy change (TEC). The calculated maximum magnetic entropy change ($-\Delta S_{M\max}$), RCP, and TEC(10) with magnetic field change of 7 T along $c$ axis reach 24.02 J kg$^{-1}$ K$^{-1}$, 378.4 J kg$^{-1}$, and 21.39 J kg$^{-1}$ K$^{-1}$ near $T_{TbC}$, which is the largest among RMn$_2$Ge$_2$ families. More importantly, this giant MCE shows plateau behavior with wide window temperatures from 93 to 108 K, making it be an attractive candidate for magnetic refrigeration applications.

Magnetocaloric effect (MCE) is the phenomenon which converts magnetic energy into thermal energy by changing the applied magnetic field$^1$–$^6$. Based on the MCE, magnetic refrigeration technology is proposed, and it has attracted great attention due to the high energy efficiency and environmental friendliness. The MCE can be quantified by adiabatic temperature change or isothermal magnetic entropy change ($-\Delta S_M$) for a certain magnetic field variation$^1$–$^6$. Up to date, numerous magnetic refrigeration materials with giant $-\Delta S_M$ accompanied by first order phase transition have been reported$^5$, $^6$. Although the MCE is intrinsic for all magnetic materials, only some of them which have strong MCE and small hysteresis loss are desirable for practical application$^1$. In addition, giant reversible MCE only appears in a narrow temperature range for most of the existing magnetic refrigeration materials. Therefore, it is important to search for materials that exhibit giant MCE not only with small hysteresis loss but also with a wide temperature range.

The ternary intermetallic compounds with the formula of RT$_2$X$_2$ (R = rare earth, T = transition metal, and X = Si, Ge) have been extensively studied due to superconductivity, magnetic ordering, and heavy-fermion properties$^7$. During the last few years, the compounds have also been found to possess giant MCE with small hysteresis loss near the magnetic ordering temperature$^8$–$^{12}$. They crystallize in ThCr$_2$Si$_2$-type tetragonal structure with space group $I4/mmm$. As shown in Fig. 1a, the structure consists of R, X, and T layers which alternately stack along c axis, and the R, T, and X atoms occupy 2$a$, 4$d$, and 4$e$ positions, respectively$^7$. In this series, special attention has been devoted to RMn$_2$X$_2$ compounds because of the magnetic Mn sublattices$^{11,12,13,14}$$. They present a vast variety of magnetic structures and magnetic phase transitions, and the magnetic state can be selected by controlling the interlayer and intralayer distance between the magnetic atoms$^{11,12}$. Very recently, the RMn$_2$Ge$_2$ compounds have triggered renewed interests due to the nontrivial transport behaviors, such as the spontaneous...
skyrmions and the giant topological Hall effect. From the results of magnetization measurement in single crystal samples, significant change in magnetization is obtained during the magnetic transition. For example, a spin reorientation of Mn moments is observed at 215 K for \( \text{NdMn}_2\text{Ge}_2 \), and a rapid upturn of magnetic susceptibility from paramagnetic (PM) to ferromagnetic (FM) transition along \( c \) axis is obtained at 325 K. These features suggest that the giant MCE may be available near the magnetic transition region. Additionally, a magnetic field-induced metamagnetic transition at certain temperature has been detected in \( \text{Tb}_{1-x}\text{Y}_x\text{Mn}_2\text{Ge}_2 \). As the direction of the magnetic moment and the symmetry of the spin texture in metamagnetic transition can be easily changed by external magnetic field, sufficient low field MCE can be achieved. To clarify the intrinsic magnetic behavior and the possible application in magnetic refrigeration, it is important to investigate the magnetic properties on single crystal samples. In this work, we present a systematic study on the anisotropy magnetic property, magnetostriction, and the MCE in \( \text{TbMn}_2\text{Ge}_2 \) single crystal. Large magnetocrystalline anisotropy below the transition temperature of Tb magnetic sublattices (\( T_{\text{C1b}} \approx 95 \) K) and a field-induced metamagnetic transition above \( T_{\text{C1b}} \) are observed, and remarkable magnetostriction is accompanied by these magnetic transitions. Strikingly, giant MCE with plateau behavior in a wide window temperature near \( T_{\text{C1b}} \) is obtained for magnetic field along \( c \) axis. Moreover, a magnetic phase diagram is constructed based on the magnetic results.

### Experimental details

The \( \text{TbMn}_2\text{Ge}_2 \) single crystal was grown using an Indium flux method. The starting materials with a molar ratio of \( \text{Tb} : \text{Mn} : \text{Ge} : \text{In} = 1:2:2:20 \) were put into an alumina crucible and sealed in a quartz tube under high vacuum. During the growth process, the tube was firstly heated up to 1373 K and kept at this temperature for 12 h. Then, it was slowly cooled to 973 K with a rate of 2 K/h. Finally, to separate the single crystal from the Indium flux, the tube was taken out from the furnace at 973 K, and the Indium flux was decanted by centrifugation.

The crystal structure was checked using an x-ray diffractometer (XRD, SmartLab, Rigaku) with Cu-Kα radiation. The crystal orientation was checked using a Rigaku XtaLab-mini-II diffractometer with Mo-Kα radiation. The elemental analysis was performed on a scanning electron microscope (SEM, JSM-IT500HR, JEOL) with an energy dispersive spectrometer (EDS). The magnetic measurements were carried out using a vibrating sample magnetometer (VSM) on a physical property measurement system (PPMS, Quantum Design). The isothermal

---

**Figure 1.** (a) The crystal structure of \( \text{RT}_2\text{X}_2 \) compounds. The green, grey, and purple balls represent the R, X, and T atoms, respectively. (b) Room-temperature powder XRD patterns of \( \text{TbMn}_2\text{Ge}_2 \). (c) The representative photograph of \( \text{TbMn}_2\text{Ge}_2 \) single crystal. (d) Room-temperature XRD patterns for \( \text{TbMn}_2\text{Ge}_2 \) single crystal recorded on (001) plane.
magnetization curves for calculating the $-\Delta S_M$ were measured in discrete steps from 90 to 115 K with temperature interval of 0.5 K, and the sample was heated to the PM temperature region and demagnetized in oscillatory mode before each measurement$^{29}$. To eliminate the influence of demagnetizing field, the demagnetization correction was performed below, and the effective field was estimated by subtracting the demagnetization field from the external field ($\mu_0 H_{\text{ext}}$) using the equation $\mu_0 H = \mu_0 (H_{\text{ext}} - N_d M)$, where $N_d$ is the demagnetization factor$^{29}$. The $N_d$ is calculated to be 0.1085 and 0.6629 along $a$ and $c$ axes, respectively. All the results were discussed based on the data after the demagnetization correction. The magnetostriction was measured using a strain gauge (KFLB, Kyowa) based on Wheatstone bridge principle, and the imbalance of the bridge was measured using a lock-in amplifier (SR830, Stanford Research Systems).

Results and discussion

The room-temperature powder XRD pattern of TbMnGe$_2$ is shown in Fig. 1b. The diffraction peaks can be well fitted with the tetragonal structure$^7$, which confirms high purity of the prepared sample. The stoichiometry ratio of Tb, Mn, and Ge is estimated to be 20.82:39.47:39.71 from the EDS results, indicating the spatially uniform stoichiometry of TbMnGe$_2$. The possible changes in magnetic structure may change is measured around the magnetic transition region. As shown in Fig. 2e, a sharp step in the relative length step moves to higher temperature, and it coincides with the magnetic transition in the inset of Fig. 2b. Based on the Rietveld analysis of neutron diffraction spectra$^{21}$, it is found that a variation of the Mn magnetic moment, $\Delta M$, is correlated with the spin configuration of Mn. When the magnetic field is applied along $c$ axis, the metamagnetic transition results in the change of Mn spin configuration. This process would induce the anomaly of $a$ cell parameter. Our results agree well with the neutron diffraction data, but a slightly lower $\Delta S_M$ is obtained. To investigate the possible coupling between the magnetic ordering and the structural parameter, the strain change is measured around the magnetic transition region. As shown in Fig. 2e, a sharp step in the relative length change ($\Delta L/L$) is observed along $a$ axis at $T_C = 2.4$ T, indicating field-induced metamagnetic transition. Due to the fact that the spin of Tb atoms is disordered above $T_C$, the tensile strain points to the spontaneous moment configuration in TbMn$_2$Ge$_2$. As shown in Fig. 2b, $T_C$ increases with decreasing temperature, and it coincides with the magnetic transition in the inset of Fig. 2b. The magnetic transition results in the change of Mn spin configuration. This process would induce the anomaly in $a$ cell parameter. Our results agree well with the data in polycrystalline TbMn$_2$Ge$_2$.$^{21,23}$ The field dependence of

The room-temperature powder XRD pattern of TbMnGe$_2$ is shown in Fig. 1b. The diffraction peaks can be well fitted with the tetragonal structure, which confirms high purity of the prepared sample. The stoichiometry ratio of Tb, Mn, and Ge is estimated to be 20.82:39.47:39.71 from the EDS results, indicating the spatially uniform stoichiometry of TbMnGe$_2$. The possible changes in magnetic structure may change is measured around the magnetic transition region. As shown in Fig. 2e, a sharp step in the relative length step moves to higher temperature, and it coincides with the magnetic transition in the inset of Fig. 2b. Based on the Rietveld analysis of neutron diffraction spectra, it is found that a variation of the Mn magnetic moment, $\Delta M$, is correlated with the spin configuration of Mn. When the magnetic field is applied along $c$ axis, the metamagnetic transition results in the change of Mn spin configuration. This process would induce the anomaly of $a$ cell parameter. Our results agree well with the neutron diffraction data, but a slightly lower $\Delta S_M$ is obtained. To investigate the possible coupling between the magnetic ordering and the structural parameter, the strain change is measured around the magnetic transition region. As shown in Fig. 2e, a sharp step in the relative length change ($\Delta L/L$) is observed along $a$ axis at $T_C = 2.4$ T, indicating field-induced metamagnetic transition. Due to the fact that the spin of Tb atoms is disordered above $T_C$, the tensile strain points to the spontaneous moment configuration in TbMn$_2$Ge$_2$. As shown in Fig. 2b, $T_C$ increases with decreasing temperature, and it coincides with the magnetic transition in the inset of Fig. 2b. The magnetic transition results in the change of Mn spin configuration. This process would induce the anomaly in $a$ cell parameter. Our results agree well with the data in polycrystalline TbMn$_2$Ge$_2$.
ΔL/L along a axis with μ0H // c is shown in Fig. 2f. It is obvious that a visible change of ΔL/L is observed at a critical field (μ0H′C), and the μ0H′C increases with increasing temperature, suggesting remarkable magnetostriction effect. When the magnetic field is applied along a axis, the field-induced anomalies are unavailable (see Fig. S3 in supplementary material for details). The strong response of the lattice to the external magnetic field indicates an unusually large coupling of the Mn magnetic moments to the lattice.

As significant changes in magnetization are obtained near the magnetic transition region in TbMn2Ge2 single crystal, giant MCE is expected, especially for μ0H//c axis. It is well known that giant MCE have a strong correlation with the first order magnetic phase transition, so it is necessary to understand the nature of the magnetic transition in TbMn2Ge2 single crystal. Figure 3a,b show the isothermal initial magnetization curves with the magnetic field along a and c axes from 3 to 115 K with an interval temperature of 0.5 K. For μ0H//a, a continuous increase in the magnetization is observed at each temperature, and the magnetization increases slightly with the increase of temperature (Fig. 3a). While for μ0H//c, the magnetization gets saturated below 0.5 T
magnetic field at 90 K (Fig. 3b). When the temperature reaches 95 K, the metamagnetic transition emerges. At lower temperature, the AFM anisotropy is weak and only a small magnetic field is required to fully polarize the spins along $c$ axis. The $\mu_0 H_C$ of the metamagnetic transition gradually increases with the increase of temperature. According to Banerjee criterion, the magnetic transition belongs to second order if all the $\mu_0 H/M$ vs $M^2$ curves (also named as Arrott plot) have positive slope. On the other hand, if some of the $\mu_0 H/M$ vs $M^2$ curves show negative slope at some points, the magnetic transition is of the first order. The Arrott plot for $\mu_0 H//a$ and $\mu_0 H//c$ are shown in Fig. 3c,d, respectively. Clearly, negative slope can be observed in the Arrott plot in Fig. 3d, indicating the occurrence of first order magnetic transition.

Based on the classical thermodynamical and the Maxwell thermodynamic relations, the $-\Delta S_M$ is given by:

$$ -\Delta S_M = \int_0^\Delta H \left[ \frac{\partial S(T,H)}{\partial H} \right]_T dH = \int_0^H \left[ \frac{\partial M(T,H)}{\partial T} \right]_H dH,$$

where $[\partial S(T,H)/\partial H]_T = [\partial M(T,H)/\partial T]_H$ is based on the Maxwell relation. For magnetization measured at small temperature and field intervals, Eq. (1) can be rewritten as:

$$ -\Delta S_M = \int_0^\Delta H M(T_{i+1},H) dH - \int_0^\Delta H M(T_i,H) dH.$$  

The temperature dependence of the calculated $-\Delta S_M$ using Eq. (2) with various magnetic field changes ($\Delta \mu_0 H$) along $a$ and $c$ axes are shown in Fig. 4a,b, respectively. For $\Delta \mu_0 H//a$, an inverse MCE with maximum magnetic entropy change ($-\Delta S_M^{\text{max}}$) of $-1.64$ J kg$^{-1}$ K$^{-1}$ is obtained near $T_C^a$, and the inverse MCE could be attributed to the magnetic transition of Tb sublattices from disorder to order along $c$ axis, which induces a slight increase of magnetization along $a$ axis. In contrast, a normal MCE is obtained for the magnetic field along $c$ axis, and the $-\Delta S_M^{\text{max}}$ is evaluated to be $24.02$ J kg$^{-1}$ K$^{-1}$ with $\Delta \mu_0 H = 7$ T at $T_C^c$, exhibiting giant MCE. The other significant feature in Fig. 4b is that a plateau behavior for the giant MCE is obtained with larger $\Delta \mu_0 H$, resulting in a wide temperature range with large $-\Delta S_M$. The peak width determined from the difference between the extreme values in the $\Delta S_M/dT$ vs $T$ curves is proportional to $\Delta \mu_0 H$, and it reaches up to 16 K with $\Delta \mu_0 H = 7$ T. For $\Delta \mu_0 H = 5$ T, the $-\Delta S_M^{\text{max}}$ is evaluated to be $23.23$ J kg$^{-1}$ K$^{-1}$. As shown in Fig. 4c, this value is much larger than that in TbMn$_2$Ge$_2$ polycrystal sample and other RMn$_2$Ge$_2$ compounds. Meanwhile, it is comparable.
with the series of $RT_2X_2$ compounds with giant MCE$^{8-12}$. Moreover, the temperature of $-\Delta S_M^\text{max}$ appears at 95 K for present sample, which is much higher than the values in above-mentioned compounds.

Figure 4d shows the $\Delta \mu_0 H$ dependence of $-\Delta S_M^\text{max}$ for $\mu_0 H//c$. The value of $-\Delta S_M^\text{max}$ increases rapidly with increasing $\Delta \mu_0 H$ from 0 to 1 T, and then it gets saturate gradually. For the relatively small value of $\Delta \mu_0 H$, the $-\Delta S_M^\text{max}$ reaches up to 20.69 J kg$^{-1}$ K$^{-1}$ ($\Delta \mu_0 H = 1$ T), suggesting giant low field MCE. Except for the $-\Delta S_M$ parameter, the relative cooling power (RCP) is also usually used to characterize the potential MCE of materials, which indicates the amount of heat transfer between the cold and hot reservoirs in an ideal refrigeration cycle$^6$. It is given by:

$$\text{RCP} = -\Delta S_M^\text{max} \delta T_{\text{FWHM}},$$  \hspace{1cm} (3)
where FWHM means the full width at half maximum in $\Delta S_M$ curve. The variation of RCP is consistent with that of $-\Delta S_M$. As shown in the inset of Fig. 4d, for $\Delta H$ larger than 1 T, both of $-\Delta S_M$ and RCP parameters can be well fitted using the power law relations: $-\Delta S_M^\text{max} = a + b(\mu_0 H)^n$ and RCP $= c + d(\mu_0 H)^n$, and the fitting yields the values of $a$, $b$, $m$, $c$, $d$, and $n$ to be 20.52, 0.132, 0.770, $-61.14$, 20.564, and 0.722. For TbMn$_2$Ge$_2$ single crystal, the RCP reaches a maximum value of 378.4 J kg$^{-1}$ with $\Delta H = 7$ T along c axis, which is of the same order of magnitude as other high-performing magnetic refrigeration materials\cite{50, 51}. Considering that the RCP tends to overestimate the merit of materials, temperature-averaged entropy change (TEC) has recently been proposed as a more predictive figure of merit to identify the performance of the MCE materials, and it can be determined using the equation\cite{50}:

$$\text{TEC(}\Delta T_{\text{lift}}\text{)} = \frac{1}{\Delta T_{\text{lift}}} \max \left\{ \frac{T_{\text{mid}} + T_{\text{mid}}^\prime}{2}, \int_{T_{\text{mid}} - \Delta T_{\text{lift}}}^{T_{\text{mid}} + \Delta T_{\text{lift}}} \Delta S(T) dH dT \right\}, \quad (4)$$

where $\Delta T_{\text{lift}}$ is the desired temperature span of the device, and $T_{\text{mid}}$ is the temperature at the center of the average that maximizes TEC($\Delta T_{\text{lift}}$) for the given $\Delta T_{\text{lift}}$. Figure 4e shows the variation of TEC with $\Delta T_{\text{lift}}$ for the magnetic field along c axis. It is seen that the TEC decreases with increasing $\Delta T_{\text{lift}}$. The value of TEC($\Delta T_{\text{lift}}= 10$ K) increases continuously and reaches 21.39 J kg$^{-1}$ K$^{-1}$ with $\mu_0 H = 7$ T. The values of TEC($\Delta T_{\text{lift}}= 3$ and 10 K) are also comparable to the previous works, such as La(Fe$_{0.88}$Si$_{0.12}$)$_3$\cite{50} and HoNiGe$_3$\cite{51}.

Based on above results, a phase diagram represented by the contour plot of $d\Delta S_M/dH$ vs $\mu_0 H$ curves is constructed for TbMn$_2$Ge$_2$ single crystal, and the data are shown in Fig. 4f. When $T_{TB}^\text{临界} < T < T_{TB}^{\text{临界}}$ the AFil-type magnetic structure is formed, and the spin alignment of adjacent Mn layers (interlayer) is antiparallel along c axis (right inset of Fig. 4f). Below $T_{TB}^{\text{临界}}$ the Tb atoms order ferromagnetically along c axis and antiferromagnetically to the Mn sublattices (left inset of Fig. 4f). The magnetic ordering of Tb atoms accompanied by the magnetostriction effect is the mainly origin of the giant MCE. Additionally, the fully polarized FM state of Mn sublattices is established above the $\mu_0 H_{c2}$, where $T > T_{TB}^{\text{临界}}$ (the middle inset of Fig. 4f). The coincidence of $\mu_0 H_{c2}$ and $\mu_0 H_{c1}^\prime$ curves implies that the remarkable magnetostriction effect is mainly due to the field-induced metamagnetic transition. The magnetic transition from AFil to FM state of Mn sublattices leads to the plateau behavior of $-\Delta S_M$ curves, and the giant MCE still retains without the ordering of Tb atoms. Further investigation of the magnetic structure evolution based on high magnetic field and neutron scattering measurement in TbMn$_2$Ge$_2$ single crystal is required to refine the phase diagram.

Conclusions
IN summary, we have studied the anisotropic magnetic property, magnetostriction, and the MCE in TbMn$_2$Ge$_2$ single crystal with the magnetic field along a and c axes. The magnetic ordering of Tb and Mn atoms results in the anomaly of $\Delta L/L$ and giant MCE near $T_{TB}$. A magnetic field-induced metamagnetic transition is observed along c axis above $T_{TB}^{\text{临界}}$, which leads to the magnetostriction effect and the plateau behavior of the MCE over a wide temperature range. The calculated results of $-\Delta S_M^\text{max}$, RCP, and TEC(10) with the values of 24.02 J kg$^{-1}$ K$^{-1}$, 378.4 J kg$^{-1}$ and 21.39 J kg$^{-1}$ K$^{-1}$ indicate that TbMn$_2$Ge$_2$ single crystal would be a promising candidate material for cryomagnetic refrigeration. Moreover, a $\mu_0 H-T$ phase diagram is established based on the magnetic behavior. The present results may provide some clue for searching novel magnetic refrigeration materials, and more studies need to be carried out to achieve a trade-off between the performance and cost, e.g., doping with light rare earth elements. Meanwhile, the temperature range where the MCE occurs needs to be further increased.

Data availability
The datasets generated and/or analysed during the current study are available in the [Crystallography Open Database] repository, [3000405].

Received: 25 July 2022; Accepted: 3 November 2022
Published online: 04 November 2022

References
1. Shen, B. G., Sun, J. R., Hu, F. X., Zhang, H. W. & Cheng, Z. H. Recent progress in exploring magnetocaloric materials. Adv. Mater. 21, 4545–4564 (2009).
2. Smith, A. et al. Materials challenges for high performance magnetocaloric refrigeration devices. Adv. Energy Mater. 2, 1288–1318 (2012).
3. Franco, V., Blázquez, J. S., Ingale, B. & Conde, A. The magnetocaloric effect and magnetic refrigeration near room temperature: Materials and models. Annu. Rev. Mater. Res. 42, 305–342 (2012).
4. Balli, M., Jandl, S., Fournier, P. & Kedous-Lebouc, A. Advanced materials for magnetic cooling: Fundamentals and practical aspects. Appl. Phys. Rev. 4, 021305 (2017).
5. Lysygin, I. Magnetocaloric materials for energy efficient cooling. J. Phys. D Appl. Phys. 50, 053002 (2017).
6. Franco, V. et al. Magnetocaloric effect: From materials research to refrigeration devices. Prog. Mater. Sci. 93, 112–232 (2018).
7. Szytula, A. & Leciejewicz, J. Magnetic properties of ternary intermetallic compounds of the RT$_2$X$_2$ type. Handb. Phys. Chem. Rare Earths 12, 133–211 (1989).
8. Li, L. et al. Low-field giant reversible magnetocaloric effect in intermetallic compound ErCr$_2$Si$_2$. Scripta Mater. 67, 237–240 (2012).
9. Mo, Z. J. et al. Magnetic properties and magnetocaloric effect in the RCu$_2$Si$_2$ and RCu$_2$Ge$_2$ (R = Ho, Er) compounds. J. Appl. Phys. 115, 073905 (2014).
10. Zuo, W. L., Hu, F. X., Sun, J. R. & Shen, B. G. Low-field large reversible magnetocaloric effect in the RNi$_2$Si$_2$ (R = Dy, Ho, Er) compounds. J. Magn. Magn. Mater. 344, 96–100 (2013).
37. Kim, J. W.

18. Kumar, P.

29. Sampathkumaran, E. V., Paulose, P. L. & Mallik, R. Magnetoresistance anomalies and multiple magnetic transitions in SmMn2Ge2.

23. Morellon, L., Arnold, Z., Kamarád, J., Ibarra, M. R. & Algarabel, P. A. The magnetic phase transitions and related volume changes.

42. Xu, L. M.

40. Zheng, X. M.

25. Hofmann, M., Campbell, S. J. & Edge, A. V. J. EuMn2Ge2 and EuMn2Si2: Magnetic structures and valence transitions.

13. van Dover, R. B.

41. Wang, S. B.

46. Caron, L.

48. Elerman, Y.

33. Fang, C. S.

39. Gong, G. G.

30. Mukherjee, K., Iyer, K. K. & Sampathkumaran, E. V. Ferromagnetic feature from Mn near room temperature in the fine particles with LaMn2Ge2.

50. Griffith, L. D., Mudryk, Y., Slaughter, J. & Pecharsky, V. K. Material-based figure of merit for caloric materials.

51. Zhao, X. W.

Acknowledgements

This work is supported by the Young Scientists Fund of the National Natural Science Foundation of China (Grant No. 11704091), the Open Project of Guangxi Key Laboratory of Nuclear Physics and Nuclear Technology (Grant No. NLK2021-10), and the Open Project of Key Laboratory of Novel Materials for Sensor of Zhejiang Province (Grant No. ZJKLNS2021010).
Author contributions
S.H. and Z.M.T. designed the experiments. Y.M.B. synthesized the single crystals. K.Q.W. performed X-ray diffraction measurements. S.H. and D.X.H. carried out measurements of physical properties. S.H. and Z.M.T. analyzed the data and prepared the manuscript. All the authors have read and approved the final version of the manuscript.

Competing interests
The authors declare no competing interests.

Additional information
Supplementary Information The online version contains supplementary material available at https://doi.org/10.1038/s41598-022-23661-4.

Correspondence and requests for materials should be addressed to S.H. or Z.T.

Reprints and permissions information is available at www.nature.com/reprints.

Publisher’s note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes were made. The images or other third party material in this article are included in the article’s Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article’s Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this licence, visit http://creativecommons.org/licenses/by/4.0/.

© The Author(s) 2022