New insight into magneto-structural phase transitions in layered TbMn$_2$Ge$_2$-based compounds

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The Tb$_{1−x}$Y$_x$Mn$_2$Ge$_2$ series ($x = 0, 0.1, 0.2$) compounds are found to exhibit two magnetic phase transitions with decreasing temperature: from the paramagnetic state to the antiferromagnetic interlayer state at $T_N^{\text{inter}}$ and from an antiferromagnetic interlayer structure to a collinear ferrimagnetic interlayer structure at $T_C^{\text{inter}}$. Compared with the slight change of $T_N^{\text{inter}}$ ($409$ K, $410$ K and $417$ K for $x = 0$, $0.1$ and $0.2$ respectively), the replacement of Y for Tb leads to a significant decrease in $T_C^{\text{inter}}$ from $97.5$ K for $x = 0$ to $74.6$ K for $x = 0.2$. The variation in $T_C^{\text{inter}}$ can be ascribed to the combination of two effects: (1) chemical pressure and (2) magnetic dilution effect by Y substitution for Tb. Besides, a strong anisotropic magnet-volume effect has been detected around $T_C^{\text{inter}}$ in all compounds with $\Delta a/a = 0.125\%$, $0.124\%$ and $0.130\%$ for $x = 0$, $0.1$ and $0.2$, respectively while no obvious effect is detected along the c-axis.

The maximum magnetic entropy change were found to be $−\Delta S_{\text{max}} = 9.1$ J kg$^{-1}$ K$^{-1}$, $11.9$ J kg$^{-1}$ K$^{-1}$ and $6.3$ J kg$^{-1}$ K$^{-1}$ with a field change from 0 T to 5 T for $x = 0$, $0.1$, $0.2$ respectively.

Since the discovery in 1997 of a giant magnetocaloric effect (GMCE) originating from a discontinuous first order magnetic transition in Gd$_3$Si$_2$Ge$_2$-1, room-temperature magnetic refrigeration based on the magnetocaloric effect (MCE) has attracted significant attention due to its energy efficiency and environmental friendly in comparison with conventional gas compression-expansion refrigeration2. A number of materials which exhibit giant magnetic entropy changes at magnetic transitions have been investigated, including MnFeP$_{0.45}$As$_{0.55}$-2, Mn$_2$As$_4$-3, MnAs$_4$-4, Sb$_5$-5, Ni-Mn-Sn-based alloys-6,7, and La(Fe,Si)$_{13}$-8. The key features of these systems are the temperature- and magnetic field-induced first-order magneto-structural or magneto-elastic phase transitions. Given these promising developments, magnetic materials which exhibit a large magnetocaloric effect have been studied extensively, both experimentally and theoretically, over the past two decades with the overall aim of increasing the efficiency of magnetic refrigeration techniques9,10. While a key focus is exploration of materials that exhibit a pronounced magnetocaloric effect at room temperature, materials that operate in the low temperature region are also useful in meeting the cooling requirements for fields such as gas liquefaction or attaining millikelvin for experimental research facilities. However, so far only a few materials such as GdLiF$_4$, GdF$_3$ and Gd$_3$Ga$_5$O$_{12}$ are used commercially11. As reflected by the increase in exploration of materials which exhibit a large MCE below room temperature10-13, the search for materials which exhibit large magnetocaloric effects over temperature ranges relevant for hydrogen and natural gas liquefaction are also important for exploring potential applications.

Some RT$_2$X$_2$ compounds (R = rare earth, T = transition metal, and X = Si or Ge) have been found to exhibit large MCE values with small hysteresis losses near their low magnetic transition temperatures14-16. For example, the magnetic entropy values of RNi$_2$Si$_2$ (R = Dy, Ho, Er) compounds are 21.3 J kg$^{-1}$ K$^{-1}$, 21.7 J kg$^{-1}$ K$^{-1}$ and 22.9 J kg$^{-1}$ K$^{-1}$ around 6.5 K, 4.5 K and 3.5 K respectively during a change of magnetic induction intensity from

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0–5 T\(^{14}\), while the magnetic entropy of ErCr\(_2\)Si, attained 29.7 J kg\(^{-1}\) K\(^{-1}\) near the magnetic ordering temperature 4.5 K\(^{17}\). The crystal structure of the RT\(_2\)X\(_2\) series is body centred tetragonal ThCr\(_2\)Si\(_2\)-type (space group I4/mmm\(^{15,18}\)) with the sequence -R-X-T-X-R- atomic layers stacked along the c-axis. The rare earth elements typically exhibit large magnetic moment (for example \(\mu_{\text{B}} = 8.8\mu_{\text{B}}\) in TbMn\(_2\)Si\(_2\) at 5 K\(^{36}\)) and correspondingly make a large contribution to the magnetocaloric effect\(^{14,15,17}\). Given the sensitivity of the magnetic state in RMn\(_2\)X\(_2\) through external factors such as pressure\(^{28}\), temperature and magnetic field\(^{29}\) meaning that such compounds have the potential for competitive performance\(^{15,19,24}\). The notations used in this paper to describe the magnetic structure type and critical transition temperatures are defined by Venturini et al.\(^{22}\) Using standard magnetic methods\(^{19,30}\), TbMn\(_2\)Ge\(_2\) was reported to be antiferromagnetic below Néel temperature \(T_N = 410\) K with the AFM antiferromagnetic interlayer structure (i.e. a collinear antiferromagnetic structure between adjacent Mn planes in a + − + − sequence along the c-axis\(^{22}\).) Below \(T_C = 100\) K, TbMn\(_2\)Ge\(_2\) exhibits a collinear ferromagnetic structure in which the Tb moments order ferromagnetically and couple antiferromagnetically with the Mn moments\(^{23}\). Furthermore, in a later study for the Tb\(_{1−x}\)Y\(_x\)Mn\(_2\)Ge\(_2\) series (x = 0–0.4), it was reported that the replacement of Y for Tb leads to significant modifications of both the Curie temperature (from 76 K for TbMn\(_2\)Si\(_2\) to almost 0 K\(^{30}\) for Tb\(_{0.5}\)Y\(_{0.5}\)Mn\(_2\)Ge\(_2\)) and magnetovolume effect (the volume effect is \(\Delta V/V = 3.2 \times 10^{-3}\) and \(2.7 \times 10^{-3}\) for x = 0 and 0.1 respectively\(^{30}\)). The magnetic phase transitions around \(T_C\) in the Tb-rich Tb\(_{1−x}\)Y\(_x\)Mn\(_2\)Ge\(_2\) compounds were shown to be first order\(^{31}\), offering scope for large magnetocaloric effects around the region of their Curie temperatures.

Here we present a systematic study of the magnetic transition from antiferromagnetism to ferromagnetism in a series of Tb\(_{1−x}\)Y\(_x\)Mn\(_2\)Ge\(_2\) samples (x = 0, 0.1, 0.2) using a combination of methods including variable temperature x-ray diffraction (XRD), specific heat, differential scanning calorimetry (DSC) and magnetization measurements. The overall aim is to understand fully the influence of Y substitution for Tb on magnetocaloric effects and search for novel magnetocaloric materials that may be suitable for operation over the hydrogen and natural gas liquefaction temperature ranges.

Method
The polycrystalline Tb\(_{1−x}\)Y\(_x\)Mn\(_2\)Ge\(_2\) samples with x = 0, 0.1, 0.2 were prepared by arc melting constituent elements of 99.9% purity under argon atmosphere. For improved crystallization and chemical homogeneity, the samples were annealed in vacuum-sealed quartz tube at 850 °C for 7 days after arc melting. The dc magnetic measurements were performed using a Quantum Design 9 T physical properties measurement system (PPMS). The magnetic behaviour was investigated over the range from 5 K to 340 K in a magnetic field 0.01 T. Differential scanning calorimetry measurements were performed on differential scanning calorimetry equipment (DSC 204 F1 Phoenix\(^{®}\)) from 340 K to 500 K. Magnetization-field loops were obtained at temperatures close to the Curie temperature of samples with magnetic fields over the range 0–5 T. The heat capacity measurements were performed on a Quantum Design 14 T physical properties measurement system scanning from 2 K to 250 K. The samples were characterized and the structures determined by variable temperatures XRD measurements over the temperature range (12–300 K) using a PANalytical diffractometer with Cu-K\(\alpha\) radiation.

Results and Discussion
Structural behaviour.
The room temperature x-ray diffraction study shows that all samples are single phase and that patterns can be indexed with a space group of I4/mmm as expected. The Rietveld refinements have been carried out using the FullProf package\(^{32}\) with the main results shown in Fig. 1(a,b and c) for x = 0, 0.1 and 0.2 respectively. It can be seen from Fig. 1. that the variations of lattice parameters of a and c with temperature display strong anisotropy: the lattice parameter a increases monotonically with increasing temperature while a pronounced discontinuity is observed in the a lattice parameter (black solid square) around the Curie temperature \(T_C\) for each sample (the transition temperatures were determined as the point where the value of dM/dT is minimum). Similar behaviours for TbMn\(_2\)Ge\(_2\) were also determined by Morellon et al.\(^{23}\) for which an anomaly in the thermal expansion along the a-axis was found near \(T_C\) (red solid circle) increases monotonically with increasing temperature while the dimensional expansion in the c direction (as derived from our specific heat measurements for each of the samples as described below for the three compositions):

\[
\beta = k\gamma C_v/V
\]

where \(\beta\) is the volume thermal expansion coefficient of the parameter state, k is the compressibility, \(\gamma\) is the Gruneisen constant and \(C_v\) is the specific heat at constant volume caused by lattice vibrations. \(C_v\) was derived from the Debye theory of specific heat using the value of the Debye temperature \(\theta_D\) (as derived from our specific heat measurements for each of the samples as described below for the three compositions):

\[
C_v = \frac{9Nk_B}{6\pi^2} \left( \frac{T}{\theta_B} \right)^3 \int_0^{\theta_B/T} \frac{x^4 e^x}{(e^x - 1)^2} dx
\]

\(0\)
where $k_B$ is the Boltzmann constant and $N$ is the number of the atoms. The thermal expansion for the hypothetical paramagnetic state is derived on integrating Eq. (2) with respect to temperature. The parameter $\gamma k_B/V$ was adjusted to obtain the best least-squares fitting to the successive data points of the observed thermal expansion curve well above the magnetic ordering temperature (based on the fact that the magnetic contribution in the antiferromagnetic region to total thermal expansion can be ignored for these types of compounds$^{32}$).

The temperature dependence of the unit cell volumes based on Debye theory for the TbMn$_2$Ge$_2$, Tb$_{0.9}$Y$_{0.1}$Mn$_2$Ge$_2$ and Tb$_{0.8}$Y$_{0.2}$Mn$_2$Ge$_2$ samples are shown by the dashed lines in Fig. 1(a, b and c) with pronounced magneto-volume effects evident below their magnetic transition temperatures $T_C = 94$ K, $T_C = 83$ K and $T_C = 70$ K respectively. The discontinuous nature of the changes in $a$ lattice parameter and unit cell volume $V$ at the Curie

Figure 1. Temperature dependence of the lattice constants $a$, $c$ and unit cell volume: (a) TbMn$_2$Ge$_2$, (b) Tb$_{0.9}$Y$_{0.1}$Mn$_2$Ge$_2$ and (c) Tb$_{0.8}$Y$_{0.2}$Mn$_2$Ge$_2$. The dashed lines show the phonon contribution to the lattice expansion as evaluated from the Gruneisen relation.
temperatures as shown in Fig. 1, are consistent with the first order nature of these transitions as discussed fully below. The changes in the lattice parameter \( a \) are \( \Delta a/a = 0.125\% \), \( \Delta a/a = 0.124\% \) and \( \Delta a/a = 0.130\% \) for \( x = 0, 0.1 \) and 0.2 respectively with spontaneous volume magnetostriction \( \omega = (\Delta V_s/V) \) at 5 K determined as: \( \text{TbMn}_2\text{Ge}_2 - \omega = 4.1 \times 10^{-3} \), \( \text{Tb}_{0.9}\text{Y}_{0.1}\text{Mn}_2\text{Ge}_2 - \omega = 3.2 \times 10^{-3} \) and \( \text{Tb}_{0.8}\text{Y}_{0.2}\text{Mn}_2\text{Ge}_2 - \omega = 5.8 \times 10^{-3} \).

**Magnetic phase transition.** The magnetisation of the three samples has been carried out in a field of \( B = 0.01 \) T over the temperature range 5–340 K. As in Fig. 2(a,b and c) the \( \text{TbMn}_2\text{Ge}_2, \text{Tb}_{0.9}\text{Y}_{0.1}\text{Mn}_2\text{Ge}_2 \) and \( \text{Tb}_{0.8}\text{Y}_{0.2}\text{Mn}_2\text{Ge}_2 \) samples were respectively measured on warming from 5 K in three states: after cooling in zero field (ZFC heating) and after cooling and heating in a field of \( B = 0.01 \) T (FC cooling and FC heating). As is evident from the magnetization versus temperature curves of Fig. 2(a,b and c), there is an abrupt change in magnetization at the Curie temperature \( T_C \) that marks the magnetic phase transition from a collinear antiferromagnetic (AFil) to a collinear ferrimagnetic structure along the \( c \) axis at lower temperature according to the neutron diffraction study on \( \text{TbMn}_2\text{Ge}_2 \)23. Of the three samples, \( \text{TbMn}_2\text{Ge}_2 \) has the highest \( T_C \) (warm) = 97.5 K and \( T_C \) (cool) = 93.0 K transitions respectively as determined from the FC heating and cooling M-T curves, while the values for \( \text{Tb}_{0.9}\text{Y}_{0.1}\text{Mn}_2\text{Ge}_2 \) are derived to be \( T_C \) (warm) = 87.5 K and \( T_C \) (cool) = 81.8 K with the values for \( \text{Tb}_{0.8}\text{Y}_{0.2}\text{Mn}_2\text{Ge}_2 \) being \( T_C \) (warm) = 74.6 K and \( T_C \) (cool) = 66.0 K (normally the transition temperature during the FC process is chosen as the Curie temperature \( T_C \)). As expected, the higher the level of doping of non-magnetic Y atoms in \( \text{Tb}_{1-x}\text{Y}_x\text{Mn}_2\text{Ge}_2 \), the lower the magnetic phase transition temperature30.

Differential scanning calorimetry measurements have been carried out on the \( \text{Tb}_{1-x}\text{Y}_x\text{Mn}_2\text{Ge}_2 \) samples under the temperature range 300–500 K (Fig. 2(d)) in order to investigate the paramagnetic to antiferromagnetic transition15,21 at \( T_C \). As revealed by the DSC results in Fig. 2(d), the \( T_C \) transition temperatures are found to increase slightly with increasing Y concentration - \( T_C \) (inter) = 409 K, \( T_C \) (inter) = 410 K and \( T_C \) (inter) = 417 K for \( x = 0.0, 0.1 \) and 0.2 respectively. Compared with the reduction in ferromagnetic transition temperature on replacement of Tb atoms by Y atoms, the paramagnetic to antiferromagnetic transition temperatures are found to exhibit a slight increase (Fig. 2). The increase in \( T_C \) (inter) values is due to enhancement of the Mn-Mn exchange interaction as a result of the slight reduction of Mn-Mn distance. This behaviour is similar to the \( \text{PrMn}_2\text{Ge}_2 - \text{Si}_x \) system36 in which the paramagnetic to antiferromagnetic transition temperatures are found to increase slightly while the antiferromagnetic to ferromagnetic transition temperatures decrease on replacing Ge with Si.

The temperature dependences of magnetization for \( \text{TbMn}_2\text{Ge}_2, \text{Tb}_{0.9}\text{Y}_{0.1}\text{Mn}_2\text{Ge}_2 \) and \( \text{Tb}_{0.8}\text{Y}_{0.2}\text{Mn}_2\text{Ge}_2 \) under various external magnetic fields are presented in Fig 3(a,b and c) respectively. As expected the ferromagnetic transition temperature \( T_C \) is shifted to higher temperature with increase in applied magnetic field. For example, the transition temperatures are \( T_C \) (inter) = 101.8 K, \( T_C \) (inter) = 92 K and \( T_C \) (inter) = 76 K for \( \text{TbMn}_2\text{Ge}_2, \text{Tb}_{0.9}\text{Y}_{0.1}\text{Mn}_2\text{Ge}_2 \) and \( \text{Tb}_{0.8}\text{Y}_{0.2}\text{Mn}_2\text{Ge}_2 \) respectively in an external magnetic field of \( B = 1 \) T, while the transition temperatures are shifted to \( T_C \) (inter) = 107 K, \( T_C \) (inter) = 98.2 K and \( T_C \) (inter) = 81 K respectively in a field of \( B = 5 \) T. The field dependences of the magnetic transition temperatures are summarized in Fig. 3(d). The values of \( dT_C/dB \) (obtained on linear fitting of the experimental data in Fig. 3(d) along with a summary of experimental data determined for \( \text{Tb}_{1-x}\text{Y}_x\text{Mn}_2\text{Ge}_2 \) (\( x = 0, 0.1, 0.2 \)) in this investigation, are provided in Table 1.

**Y doping in \( \text{Tb}_{1-x}\text{Y}_x\text{Mn}_2\text{Ge}_2 - Chemical pressure effect.** As noted above, the effect of replacing the magnetic rare earth Tb with the nonmagnetic ion Y in \( \text{Tb}_{1-x}\text{Y}_x\text{Mn}_2\text{Ge}_2 \) is to weaken the exchange interaction between magnetic ions due to the dilution effect. The magnetic behaviour of Y-doped \( \text{Tb}_{1-x}\text{Y}_x\text{Mn}_2\text{Ge}_2 \) will also be modified as a result of chemical pressure due to differences in the atomic radii of the Tb (1.80 Å) and Y (1.78 Å) ions and resultant changes in lattice parameters. In order to separate these two contributions - dilution effect and pressure effect - and their influence on the variation in magnetic transition temperature, the decrease of \( T_C \) by chemical pressure was calculated as follows. The chemical pressure \( \Delta p \) was calculated23,22,29 according to the Murnaghan equation below:

\[
\Delta p(V) = \frac{B_0}{B_0'} \left( \frac{V_0}{V} \right)^{\frac{B_0'}{B_0}} - 1
\]

where \( V_0, B_0 \) and \( B_0' \) are the volume, the bulk modulus and its first derivative of \( \text{TbMn}_2\text{Ge}_2 \) and \( V \) is the volume of the unit cell at room temperature of the Y doped samples. Here, due to the similarity of crystal structure for the \( \text{RMn}_2\text{Ge}_2 \) system, we assume that the values of \( B_0 \) and \( B_0' \) for \( \text{PrMn}_2\text{Ge}_2 \) (\( B_0 = 38.0 \) Gpa, \( B_0' = 19.5 \) as derived from our synchrotron data under external pressure38) can be applied to \( \text{TbMn}_2\text{Ge}_2 \) at room temperature. Given that the doped materials \( \text{Tb}_{1-x}\text{Y}_x\text{Mn}_2\text{Ge}_2 \) (\( x = 0, 0.1, 0.2 \)) retain the \( \text{ThCr}_2\text{Si}_2 \)-type tetragonal structure, the chemical pressure \( \Delta p \) caused by doping can be assumed to have the same effect as mechanical pressure. According to previous findings that describe the pressure effect on the magnetic properties of \( \text{TbMn}_2\text{Ge}_2 \) (\( dT_C/dp = -2.9 \) K/kbar)38, the values of \( \Delta T_C \) can be deduced by the relationship:

\[
\Delta T_C^{chemical} = \frac{dT_C}{dp} \Delta p
\]

where \( \Delta p \) is the calculated chemical pressure. The calculated values of \( \Delta T_C \) for \( \text{Tb}_{0.9}\text{Y}_{0.1}\text{Mn}_2\text{Ge}_2 \) and \( \text{Tb}_{0.8}\text{Y}_{0.2}\text{Mn}_2\text{Ge}_2 \) are \( \Delta T_C = 1.94 \) K and \( \Delta T_C = 8.7 \) K respectively. As noted above (see also Figs 1, Figs 2 and 3) the effect of replacing Tb atoms with Y atoms in \( \text{Tb}_{1-x}\text{Y}_x\text{Mn}_2\text{Ge}_2 \) also contributes to the decrease in the Curie temperature. It can therefore be concluded that chemical pressure accounts for \( \sim 17.3\% \) and \( \sim 32.2\% \) of the decrease in transition temperatures for \( x = 0.1 \) and 0.2 respectively. In addition, the value of \( dT_C/dp \) can be derived using the Clausius-Clapeyron thermodynamic relation as follows:23
Figure 2. Temperature dependence of magnetization on ZFC heating, FC cooling and FC heating processes under a field of $B = 0.01$ T: (a) TbMn$_2$Ge$_2$, (b) Tb$_{0.9}$Y$_{0.1}$Mn$_2$Ge$_2$ and (c) Tb$_{0.8}$Y$_{0.2}$Mn$_2$Ge$_2$. (d) the differential scanning calorimetry curves for the three samples over the range ~300–500 K.
Figure 3. The magnetisation versus temperature curves during cooling under various magnetic field (B = 1–5 T). (a) TbMn$_2$Ge$_2$, (b) Tb$_{0.9}$Y$_{0.1}$Mn$_2$Ge$_2$, (c) Tb$_{0.8}$Y$_{0.2}$Mn$_2$Ge$_2$. (d) The variation of ferromagnetic transition temperature $T_c$ with magnetic field for the three samples. The dashed lines represent linear fits to the $T_c$-B curves leading to $dT_c/dB$ values for each sample.
Table 1. Experimental data for the three $\text{Tb}_x \cdot \text{Y}_x \cdot \text{Mn}_2 \cdot \text{Ge}_2$ samples ($x = 0$, 0.1 and 0.2).

| $x$ | 0  | 0.1 | 0.2 |
|-----|----|-----|-----|
| $\Delta p$ (Gpa) | 0  | 0.012 | 0.053 |
| $V$ ($\text{Å}^3$) (300 K) | 173.66(5) | 173.63 | 173.53 |
| $\Delta \mu$ (Am$^2$/kg) (B = 1 T) | 14.0(5) | 28.2 | 22.7 |
| experimental $T_c$ (K) (FC) | 93.0(5) | 81.8 | 66.0 |
| $\Delta T_c$ (K) | 0  | 1.94 | 8.70 |
| $\Delta T_c$ (total) (K) | 0  | 11.2 | 27.0 |
| $\Delta T_c$ (chemical)/$\Delta T_c$ (total) | 0  | 17.3% | 32.2% |
| $dT_c/dB$ (cooling) (K/T) (FC) | 1.06 ± 0.04 | 1.54 ± 0.05 | 1.29 ± 0.09 |
| $dT_c/dp$ (K/kbar) (FC) | −3.03 | −2.84 | −3.07 |

The values of the change in the unit cell volume $\Delta V_u$, change in moment $\Delta \mu$ during magnetic phase transition around $T_c$, and $dT_c/dB$ for each sample were taken from the present experimental results listed in Table 1. The derived results are $dT_c/dp = -3.03 \text{ K/kbar}$, $-2.84 \text{ K/kbar}$ and $-3.07 \text{ K/kbar}$ for $\text{TbMn}_2 \cdot \text{Ge}_2$, $\text{Tb}_{0.9} \cdot \text{Y}_{0.1} \cdot \text{Mn}_2 \cdot \text{Ge}_2$ and $\text{Tb}_{0.8} \cdot \text{Y}_{0.2} \cdot \text{Mn}_2 \cdot \text{Ge}_2$, respectively. These calculated values are in general accord with the value of $dT_c/dp = -2.9 \text{ K/kbar}$ for $\text{TbMn}_2 \cdot \text{Ge}_2$, deviating by $-4.5\%$, $-2.1\%$ and $-5.9\%$ for the $x = 0$, 0.1, 0.2 samples respectively.

**Magnetocaloric effect.** Graphs of the magnetization as a function of applied field are shown for $\text{TbMn}_2 \cdot \text{Ge}_2$, $\text{Tb}_{0.9} \cdot \text{Y}_{0.1} \cdot \text{Mn}_2 \cdot \text{Ge}_2$, and $\text{Tb}_{0.8} \cdot \text{Y}_{0.2} \cdot \text{Mn}_2 \cdot \text{Ge}_2$ at temperatures around $T_c$ in Fig. 4a,b and c respectively. It can be seen that with increasing temperature beyond $T_c$, a field-induced metamagnetic phase transition from the antiferromagnetic state to the ferromagnetic state at certain temperatures has been detected. The region of the metamagnetic phase transition for $\text{TbMn}_2 \cdot \text{Ge}_2$ is indicated by arrows in Fig. 4a as a typical example. This behaviour indicates that the region of ferromagnetic ordering in $\text{Tb}_{1-x} \cdot \text{Y}_x \cdot \text{Mn}_2 \cdot \text{Ge}_2$ can be shifted to higher temperatures by a stronger applied magnetic field.

The nature of the magnetic transitions (first order or second order) was analysed using Arrott plots with the magnetisation expressed in the usual way as graphs of $M^2$ versus B/M (Fig. 5). As can be seen in Fig. 5a,b and c, negative slopes are detected in the $M^2$ versus B/M graphs for the $\text{TbMn}_2 \cdot \text{Ge}_2$ and $\text{Tb}_{0.9} \cdot \text{Y}_{0.1} \cdot \text{Mn}_2 \cdot \text{Ge}_2$ samples thus indicating that the antiferromagnetic to ferromagnetic processes are first order. However, some papers have reported that for compounds near the critical point (from first order to second order magnetic phase transition) such as DyCo$_2$, this criterion of Arrott plots do not always work properly. It is also noted that the negative slopes for $\text{Tb}_{0.9} \cdot \text{Y}_{0.1} \cdot \text{Mn}_2 \cdot \text{Ge}_2$ around the antiferromagnetic to ferromagnetic transition was reduced compared with those for the $\text{TbMn}_2 \cdot \text{Ge}_2$ and $\text{Tb}_{0.8} \cdot \text{Y}_{0.2} \cdot \text{Mn}_2 \cdot \text{Ge}_2$ samples. However, the first order transition characters of all the three samples can be confirmed from our variable temperatures crystal structure analyses above, where strong magneto-elastic coupling around $T_c$ has been detected (Fig. 1).

The magnetic entropy changes $\Delta S_m$ for all samples have been determined from the isothermal magnetization curves of Fig. 4a,b and c, by using the standard Maxwell relationship:

$$\Delta S_m(T, B) = \int_{B_{\text{int}}}^{B_{\text{max}}} \left(\frac{\partial M(B, T)}{\partial T}\right)_B dB.$$  

The calculated temperature dependent magnetic entropy changes for the $\text{Tb}_{1-x} \cdot \text{Y}_x \cdot \text{Mn}_2 \cdot \text{Ge}_2$ samples with $x = 0$, 0.1 and 0.2 are shown in Fig. 6a,b and c respectively with the maximum values $\Delta S_{\text{max}}$ shown as a function of applied field in the insets of Fig. 6. With a field change of $\Delta B = 0$ to 5 T, the value of $\Delta S_{\text{max}}$ are 9.1 J/kgK, 11.9 J/kgK and 6.3 J/kgK for $\text{TbMn}_2 \cdot \text{Ge}_2$, $\text{Tb}_{0.9} \cdot \text{Y}_{0.1} \cdot \text{Mn}_2 \cdot \text{Ge}_2$, and $\text{Tb}_{0.8} \cdot \text{Y}_{0.2} \cdot \text{Mn}_2 \cdot \text{Ge}_2$ respectively, demonstrating that the entropy change for $\text{Tb}_{0.9} \cdot \text{Y}_{0.1} \cdot \text{Mn}_2 \cdot \text{Ge}_2$ is the largest of the three samples. As it is clear from Fig. 4, while $\text{TbMn}_2 \cdot \text{Ge}_2$ has the highest fraction of magnetic rare earth element and largest saturation magnetization (42.5 Am$^2$/kg at 84 K), its large hysterisis loss (7.4 Am$^2$/kg) leads to reduction in the magnetic entropy change. By comparison, with the lowest concentration of magnetic rare earth Tb, the $\text{Tb}_{0.9} \cdot \text{Y}_{0.1} \cdot \text{Mn}_2 \cdot \text{Ge}_2$ sample displays the lowest saturation magnetization (only 32.5 Am$^2$/kg even at 55 K) and the smallest hysterisis loss (5.2 Am$^2$/kg), while as shown in Fig. 4b, $\text{Tb}_{0.8} \cdot \text{Y}_{0.2} \cdot \text{Mn}_2 \cdot \text{Ge}_2$ with medium concentration of Tb has a relatively large saturation magnetization of 38.0 Am$^2$/kg at 84 K and small hysterisis loss (5.36 Am$^2$/kg). The refrigerant capacity (RCP), defined as the product of $-\Delta S_{\text{max}}$ and the full width at half maximum of the $-\Delta S_{\text{max}}$ curve, for the three samples are: 93.3 J/kg, 102.9 J/kg,
62.4 J/kg for TbMn$_2$Ge$_2$, Tb$_{0.9}$Y$_{0.1}$Mn$_2$Ge$_2$ and Tb$_{0.8}$Y$_{0.2}$Mn$_2$Ge$_2$ respectively, with a field change of $\Delta B = 0$–5 T. The MCE value of Tb$_{0.9}$Y$_{0.1}$Mn$_2$Ge$_2$ is comparable to those of other materials for a field change of $\Delta B = 0$–5 T including: GdCoAl, $\Delta S_{\text{max}}(T) = 10.4$ J/kgK at 100 K$^{34}$, TbCoAl, $\Delta S_{\text{max}}(T) = 10.5$ J/kgK at 70 K$^{34}$ and GdMn$_2$Ge$_2$, $\Delta S_{\text{max}}(T) = 1.2$ J/kgK at 95 K$^{28}$, all of which, in common with Tb$_{0.9}$Y$_{0.1}$Mn$_2$Ge$_2$, importantly exhibit negligible field and thermal hysteresis losses.

Moreover, it is well accepted that first-order phase transitions are accompanied by a latent heat and the barocaloric effect can be expected. In fact giant barocaloric effect has been found in several systems recently including Mn$_3$GaN ($\Delta S_{\text{bar}} = 22.3$ J/K kg)$^{42}$ and Ni–Mn–In magnetic superelastic alloys ($\Delta S_{\text{bar}} = 27.7$ J/K kg)$^{43}$. Based on the fact that all these three Tb$_{1-x}$Y$_x$Mn$_2$Ge$_2$ samples exhibit strong magnetovolume effect around magnetic phase transition, we have calculated the barocaloric effect using the Clausius–Clapeyron relation$^{43}$. The barocaloric effects entropy change $\Delta S_{\text{bar}}$, have been derived to be 9.6 J/kgK, 13.5 J/kgK and 13.2 J/kgK for TbMn$_2$Ge$_2$, Tb$_{0.9}$Y$_{0.1}$Mn$_2$Ge$_2$ and Tb$_{0.8}$Y$_{0.2}$Mn$_2$Ge$_2$ respectively. These barocaloric values indicate that these materials can be considered as a potential candidate for mechanocaloric effects over the hydrogen and natural gas liquefaction temperature ranges.

**Heat Capacity.** The heat capacity of TbMn$_2$Ge$_2$ over the temperature range 2–250 K is shown in Fig. 7(a). The sharp peak in the heat capacity near the Curie temperature of TbMn$_2$Ge$_2$ on both zero magnetic field and a field of 2 T reflects the first order character of the magnetic phase transition. The peak in specific heat shifts from ~98 K to 102.6 K for magnetic fields of 0 T and 2 T respectively; this behaviour corresponds well to the values of the Curie temperature of TbMn$_2$Ge$_2$ - 97.5 K (B = 0 T) to 103 K (B = 2 T) - obtained for the magnetization measurements (Fig. 3(d)).

The heat capacity $C(T)$ of a metallic magnetic material includes contributions from phonons, electrons and magnons and can be described as follows:

$$C(T) = C_{\text{ph}}(T) + C_{\text{el}}(T) + C_{\text{m}}(T),$$

where $C_{\text{ph}}$, $C_{\text{el}}$ and $C_{\text{m}}$ are the lattice, electronic, and magnetic contributions respectively$^{44}$. In the absence of a magnetic phase transition, the heat capacity can be described as:

$$C(T) = \gamma T + \beta T^3,$$

where $\gamma$ and $\beta$ are the electronic and phonon heat capacity coefficients, respectively. For the specific heat of TbMn$_2$Ge$_2$ at low temperatures T $\lesssim 1$ K, well away from the magnetic transition, as shown in Fig. 7(b), a fit to the graph of $C_p/T$ versus $T^2$ leads to $\gamma = (65.2 \pm 0.95)$ mJ/molK$^2$, $\beta = (4.53 \pm 0.156) \times 10^{-4}$ J/molK$^4$. The electronic density of states N(E$_F$) at the Fermi surface can be calculated by the formula$^{44}$.
\[ \gamma = \frac{k_B^2 \pi^5}{3} N(E_F) \]  \hspace{1cm} (9)

where \( k_B \) is the Boltzmann constant. For the TbMn\(_2\)Ge\(_2\) compound, the value of \( N(E_F) \) is derived to be \((5.54 \pm 0.08)\) state/eV atom. Likewise, the Debye temperature \( \theta_D \) can also be obtained by:

\[ \beta = \frac{12 \pi^4 \times R}{5 \times \theta_D^3} \cong \frac{1944 \times n}{\theta_D^3} \]  \hspace{1cm} (10)

Figure 6. The magnetic entropy changes around the ferromagnetic transition temperatures for applied magnetic fields from 1–5 T. (a) TbMn\(_2\)Ge\(_2\), (b) Tb\(_{0.9}\)Y\(_{0.1}\)Mn\(_2\)Ge\(_2\), and (c) Tb\(_{0.8}\)Y\(_{0.2}\)Mn\(_2\)Ge\(_2\) (black full symbols ■ ■ ▲ for 1–5 T respectively during increasing field and the red empty symbols correspond to 1–5 T for the decreasing field). The insets show the variation of the maximum values of magnetic entropy changes for the decreasing field values.
where $R$ is the universal gas constant and the number of atoms $n = 5^{45}$. The Debye temperature for TbMn$_2$Ge$_2$ was determined as $\theta_D = 278 \pm 3$ K.

The magnetic entropy change, $-\Delta S_M(T, B)$ can also be derived from measurements of the in-field heat capacity using the expression thermodynamic relations below:\(^{46}\)

$$\Delta S_M(T, B) = \int_0^T \frac{C(T', B) - C(T', 0)}{T'} \,dT'$$

where $C(T, B)$ and $C(T, 0)$ are the values of the heat capacity measured in field $B$ and zero field, respectively. The maximum of magnetic entropy change has been derived to be $-\Delta S_M = 2.6$ J/kgK for TbMn$_2$Ge$_2$ (field change of $\Delta B = 2$ T), which is smaller than the value ($-\Delta S_M = 5.9$ J/kgK) deduced from the isothermal magnetization

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**Figure 7.** The specific heat capacity relative parameters for TbMn$_2$Ge$_2$. (a) The specific heat capacity $C_p$ of TbMn$_2$Ge$_2$ over the temperature range 2–250 K in zero magnetic field (red solid square) and a field of 2 T (blue solid triangle). (b) A graph of $C_p/T$ versus $T^2$ for TbMn$_2$Ge$_2$ at temperatures below 10 K. (c) Magnetic entropy change $-\Delta S$ as a function of temperature derived from the specific heat data of Fig. 7(a) for $\Delta B = 0$–2 T. The inset shows the corresponding adiabatic temperature change, $\Delta T_{ad}$. 
curves. This behaviour may be due to the fact that a straightforward numerical integration using Maxwell equation based on magnetization curves is not applicable in the phase-separated state as described in ref. 47,48. The corresponding adiabatic temperature change, $\Delta T_{ad}$ (shown as inset of Fig. 7(c) can be evaluated from $-\Delta S_M(T,B)$ and the heat capacity data.

The equivalent heat capacity parameters for Tb$_{0.9}$Y$_{0.1}$Mn$_2$Ge$_2$ and Tb$_{0.8}$Y$_{0.2}$Mn$_2$Ge$_2$ are shown in Figs 8 and 9, respectively. The Debye temperatures were found to increase from 281 K for TbMn$_2$Ge$_2$ to 344 K for Tb$_{0.9}$Y$_{0.1}$Mn$_2$Ge$_2$ and 354 K for Tb$_{0.8}$Y$_{0.2}$Mn$_2$Ge$_2$; with the increases understood in terms of the differences in their molecular mass$^{31}$. The adiabatic temperature changes near the Curie temperature are found to decrease from $-\Delta T_{ad} = 2.6$ K for TbMn$_2$Ge$_2$ to $-\Delta T_{ad} = 2.3$ K for Tb$_{0.9}$Y$_{0.1}$Mn$_2$Ge$_2$ and 1.8 K for Tb$_{0.8}$Y$_{0.2}$Mn$_2$Ge$_2$.

The electron density at the Fermi surface is found to decrease from 5.54 state/eV atom for TbMn$_2$Ge$_2$ and 2.18 state/eV atom and 3.06 state/eV atom for Tb$_{0.9}$Y$_{0.1}$Mn$_2$Ge$_2$ and Tb$_{0.8}$Y$_{0.2}$Mn$_2$Ge$_2$ respectively. All the fitting results including electronic heat capacity coefficient $\gamma$, phonon heat capacity coefficient $\beta$, electronic density of

Figure 8. The specific heat capacity relative parameters for Tb$_{0.9}$Y$_{0.1}$Mn$_2$Ge$_2$. (a) The specific heat capacity $C_p$ of Tb$_{0.9}$Y$_{0.1}$Mn$_2$Ge$_2$ over the temperature range 2–250 K in zero magnetic field (red solid square) and a field of 2 T (blue solid triangle). (b) A graph of $C_p/T$ versus $T^2$ for Tb$_{0.9}$Y$_{0.1}$Mn$_2$Ge$_2$ at temperatures below 10 K.

(c) Magnetic entropy change $-\Delta S$ as a function of temperature derived from the specific heat data of Fig. 8a for $\Delta B = 0–2$ T. The inset shows the corresponding adiabatic temperature change, $\Delta T_{ad}$. 
states N(EF) and Debye temperature $\theta_D$ are summarized in Table 2. The modification of the electron density at the Fermi surface may be related to the difference of electronic configuration of Y and Tb as well as the unit cell size variation. The latter may lead to the variation in the degree of hybridization of Mn 3d states with p states of Ge with decreasing interatomic distances for Y doped samples. Similar behaviour has been found in the La$_{1-x}$Y$_x$Mn$_2$Si$_2$ system where the electron density is derived to be 2.83 states/eV atom for $x = 0$, 2.51 states/eV atom for $x = 0.25$, 2.54 states/eV atom for $x = 0.3$ and 1.47 states/eV atom for $x = 1.0^{29}$. Moreover, it is also noted that the electron density at the Fermi level for TbMn$_2$Si$_2$ was reported to be 2.38 states/eV atom, which is close to the values reported here for Tb$_{1-x}$Y$_x$Mn$_2$Ge$_2$ samples.

**Conclusions**

In conclusion, we have carried out a detailed investigation around the region of the magnetic transitions of compounds in the Tb$_{1-x}$Y$_x$Mn$_2$Ge$_2$ series ($x = 0, 0.1, 0.2$) by variable temperature x-ray diffraction, heat capacity,
Table 2. Calculated heat capacity parameters for Tb$_{1-x}$Y$_x$Mn$_2$Ge$_2$ (x = 0, 0.1, 0.2). Electronic heat capacity coefficient $\gamma$, phonon heat capacity coefficient $\beta$, electronic density of states $N(E_F)$ and Debye temperature $\theta_D$.

| x   | $\gamma$ [mJ/(mol·K$^2$)] | $\beta$ [mJ/(mol·K$^2$)] | $N(E_F)$ (state/eV·atom) | $\theta_D$ (K) |
|-----|--------------------------|--------------------------|--------------------------|----------------|
| 0   | 65.2 ± 0.9              | (4.53 ± 0.16) x 10$^{-4}$ | 5.54 ± 0.08              | 278 ± 3 |
| 0.1 | 25.6 ± 2.0              | (2.39 ± 0.24) x 10$^{-4}$ | 2.18 ± 0.17              | 345 ± 12 |
| 0.2 | 36.0 ± 1.3              | (2.19 ± 0.19) x 10$^{-4}$ | 3.06 ± 0.11              | 355 ± 11 |

differential scanning calorimetry and magnetic measurements. Two magnetic phase transitions occur at $T_{N_{inter}}$ and $T_{C_{inter}}$ for each of the three samples. The antiferromagnetic transition at $T_{N_{inter}}$ is shown to increase slightly with increase in the Y concentration, while the ferromagnetic transition at $T_{C_{inter}}$ drops significantly. The mechanism of reduction of $T_C$ due to the substitution of Y for Tb has been analysed and chemical pressure is found to play a significant role. Moreover, the entropy change of Tb$_{0.9}$Y$_{0.1}$Mn$_2$Ge$_2$ is found to exhibit very good magnetocaloric performance around $T_{C_{inter}}$ ($-\Delta S = 11.9$ J kg$^{-1}$ K$^{-1}$ and $\Delta C_P = 102.9$ J kg$^{-1}$ K$^{-1}$ for a field change of $\Delta B = 0$–5 T) with a small hysteresis loss of 5.36 J/kg. This behaviour reflects the potential suitability of Tb$_{0.9}$Y$_{0.1}$Mn$_2$Ge$_2$ for operation as a magnetic refrigerator below the nature gas liquefaction temperature. The Debye temperature and the density of states $N(E_F)$ at the Fermi level have been determined and analyzed from the heat capacity.

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Author Contributions
J.L. Wang and Z.X. Cheng designed the project. C.S. Fang, G. X Li, J.L. Wang, W.D. Hutchison, Z.X. Cheng and Q.Y. Ren carried out the experimental work. C.S. Fang, J.L. Wang, Z.X. Cheng and S.J. Campbell wrote the paper. All the authors interpreted and discussed the work.

Additional Information
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