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Magnetic transitions and the magnetocaloric effect in the Pr $1-xYxMn_2Ge_2$ system

Abstract

Layered rare earth compounds in the RMn_2X_2 series (R = rare-earth; X = Ge, Si) are of interest for potential cooling applications at lower temperatures as they enable the structural and magnetic behavior to be controlled via substitution of R , Mn , and X atoms on the 2a, 4d, and 4e sites respectively. We continue investigations of the $Pr_{1-x}Y_xMn_2Ge_2$ magnetic phase diagram as functions of both composition and Mn-Mn spacing using X-ray and neutron diffraction, magnetization and differential scanning calorimetry measurements. $Pr_{1-x}Y_xMn_2Ge_2$ exhibits an extended region of re-entrant ferromagnetism around $x \sim 0.5$ with re-entrant ferromagnetism at inline image for $Pr_{0.5}Y_{0.5}Mn_2Ge_2$. The entropy values $-\Delta S_M$ around the ferromagnetic transition temperatures inline image from the layered antiferromagnetic AFI structure to the canted ferromagnetic structure F_{mc} (typically inline image) have been derived for $Pr_{1-x}Y_xMn_2Ge_2$ with $x = 0.0, 0.2$, and 0.5 for $\Delta B = 0-5$ T. The changes in magnetic states due to Y substitution for Pr are discussed in terms of chemical pressure, external pressure, and electronic effects.

Keywords

transitions, magnetocaloric, effect, pr, magnetic, 1, system, $xyxmn_2ge_2$

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Magnetic transitions and the magne-tocaloric effect in the $\text{Pr}_{1-x}\text{Y}_x\text{Mn}_2\text{Ge}_2$ system

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Layered rare earth compounds in the RMn_2X_2 series ($\text{R}=\text{rare-earth}$; $\text{X}=\text{Ge, Si}$) are of interest for potential cooling applications at lower temperatures as they enable the structural and magnetic behaviour to be controlled *via* substitution of R, Mn, X atoms on the 2a, 4d and 4e sites respectively. We continue investigations of the $\text{Pr}_{1-x}\text{Y}_x\text{Mn}_2\text{Ge}_2$ magnetic phase diagram as functions of both composition and Mn–Mn spacing using x-ray and neutron diffraction, magnetisation and differential scanning calorimetry measurements. $\text{Pr}_{1-x}\text{Y}_x\text{Mn}_2\text{Ge}_2$ exhibits an extended region of re-entrant ferromagnetism around

$x\sim 0.5$ with re-entrant ferromagnetism at $T_c^{\text{Pr}} \sim 50$ K for $\text{Pr}_{0.5}\text{Y}_{0.5}\text{Mn}_2\text{Ge}_2$. The entropy values $-\Delta S_M$ around the ferromagnetic transition temperatures T_c^{inter} from the layered antiferromagnetic AFI structure to the canted ferromagnetic structure *Fmc* (typically $T_c^{\text{inter}} \sim 330\text{--}340$ K) have been derived for $\text{Pr}_{1-x}\text{Y}_x\text{Mn}_2\text{Ge}_2$ with $x=0.0, 0.2$ and 0.5 for $\Delta B=0\text{--}5$ T. The changes in magnetic states due to Y substitution for Pr are discussed in terms of chemical pressure, external pressure and electronic effects.

1 Introduction

The potential for cooling materials by manipulating magnetic dipoles with applied magnetic fields is widely considered to stem from the discovery of the magnetocaloric effect in Fe by Warburg in 1881 [1]. Recently however, Smith [2] has presented a thorough assessment of the early literature surrounding the connection between magnetism and heat (see also Smith *et al.* [3]). In his overview, Smith [2] argues that discovery of the magnetocaloric effect is more correctly identified with the magnetisation studies of Ni by Weiss and Piccard in 1917 [4] in which they observe and account for the reversible temperature change of Ni around its Curie temperature. As summarised for example by Gschneidner *et al.* [5], theoretical insights of the 1920s led to the development and application of adiabatic demagnetization in the 1930s. Indeed, the advent of magnetic cooling underpins aspects of the development of low temperature physics throughout the 20th Century. A further major development occurred in 1997 with the report of a giant magnetocaloric effect (MCE) near room temperature in the layered rare earth compound $\text{Gd}_5\text{Si}_2\text{Ge}_2$ [6]. This discovery, combined with the environmental imperatives of energy efficiencies and reduction in pollution, has led to

continuing efforts in the search for materials with a large magnetocaloric effect (over 5079 papers have been published on the topics “*magnetic refrigeration*” or “*magnetocaloric effect*” since 1997 with 34 already published in 2014 [7]). The increasingly significant impact of magnetic refrigeration is also demonstrated by the fact that by 2010 over 42 laboratory-scale magnetic cooling units have been built and tested World-wide [8, 9].

The rapid change in magnetisation associated with first order magnetic transitions together with simultaneous field-induced magnetic and structural transformations lead to enhanced entropy values [10]. For example, materials based on the NiMnGa and MnCoGe systems show pronounced entropy behaviour at magnetostructural transitions around room temperature [e.g. 11, 12, 13]. Layered rare earth compounds in the RMn_2X_2 series ($\text{R}=\text{rare-earth}$; $\text{X}=\text{Ge, Si}$) are also of interest as they enable the structural and magnetic behaviour to be controlled *via* substitution of R, Mn, X atoms on the 2a, 4d and 4e sites respectively [14–19]. The overall magnetic behaviour of RMn_2Ge_2 compounds is strongly influenced by two critical values of the intralayer Mn–Mn distance $d_{\text{Mn–Mn}}^a$: $d_{\text{crit1}} = 2.87$ Å (of related lattice parameter $a_{\text{crit1}}=4.06$ Å) and $d_{\text{crit2}} = 2.84$ Å (related lattice parameter $a_{\text{crit2}}=4.02$ Å) [14, 17–

18]. For compounds with $d_{\text{Mn-Mn}}^a > d_{\text{crit1}}$, the intralayer in-plane coupling is antiferromagnetic and the interlayer coupling is ferromagnetic [14, 17-18] leading to the Fmc-type magnetic configuration.

In the case of the $\text{Pr}_{1-x}\text{Y}_x\text{Mn}_2\text{Ge}_2$ system, given that PrMn_2Ge_2 is ferromagnetic and YMn_2Ge_2 antiferromagnetic at room temperature, the $\text{Pr}_{1-x}\text{Y}_x\text{Mn}_2\text{Ge}_2$ system leads to an extended region of re-entrant ferromagnetism around $x \sim 0.5$ [18]. The combination of ferromagnetic ordering of the Pr-sublattice and ferromagnetic ordering of the Mn-sublattice in turn leads to enhanced magnetocaloric behaviour.

Here, we report extension of our studies of the structural and magnetic properties of $\text{Pr}_{1-x}\text{Y}_x\text{Mn}_2\text{Ge}_2$ using x-ray and neutron diffraction together with magnetic measurements [18-19]. Our investigations have led to construction of the magnetic phase diagram for $\text{Pr}_{1-x}\text{Y}_x\text{Mn}_2\text{Ge}_2$ as functions of both composition and the Mn-Mn spacing and exploration of the magnetic transitions and entropy changes observed at the ferromagnetic transition. The changes in magnetic states due to Y substitution for Pr are discussed in terms of chemical pressure, external pressure and electronic effects.

2 Experimental

The set of $\text{Pr}_{1-x}\text{Y}_x\text{Mn}_2\text{Ge}_2$ compounds (with $x=0.0 - 1.0$) were prepared using conventional argon arc melting. The starting materials contained $\sim 3\%$ excess Mn to compensate for the Mn loss due to evaporation during melting. The ingots were melted five times for improved homogeneity and then annealed at 900°C for one week in an evacuated quartz tube. The samples were characterized at room temperature by x-ray diffraction (CuK_α radiation, $\lambda = 1.5418 \text{ \AA}$). The temperature dependences of the DC magnetisation and the AC magnetic susceptibility were measured using a superconducting quantum interference device (SQUID) and a Quantum Design Physical Properties Measurement System (PPMS) Magnetometer from 5 K to 340 K. A search for higher temperature phase transitions in the range 300 K to 570 K was carried out using differential scanning calorimetry (DSC) at a heating rate of 10 K/min. Neutron diffraction experiments were carried out on the GEM time-of-flight diffractometer at ISIS (STFC, UK) from 30-360 K [e.g. 19] and the Echidna and Wombat diffractometers at OPAL (Australia). Rietveld refinements have been carried out using the FULLPROF program package [20] which allows simultaneous refinement of the structural and magnetic parameters.

3. Results and Discussion

X-ray Diffraction: Analysis of the room temperature x-ray diffraction (XRD) patterns of $\text{Pr}_{1-x}\text{Y}_x\text{Mn}_2\text{Ge}_2$ (Figure 1(a)) indicates that all of the samples are single phase with

the expected body-centred tetragonal ThCr_2Si_2 -type structure (space group $I4/mmm$). The lattice parameters derived from refinement of the room temperature patterns are presented in Figure 1(b) as a function of composition. The present set of lattice parameters are similar to those reported in reference [21] which are also shown in Figure 1(b). Both the a and c lattice parameters decrease linearly with increasing Y content with rates of change: $da/dx = -0.133 \text{ \AA}$ and $dc/dx = -0.053 \text{ \AA}$ respectively in accord with Vegard's Law.

With respect to PrMn_2Ge_2 as the reference, we consider the influence of the reduction in unit cell volume due to Y substitution to be analogous to the effects of "chemical pressure". The Murnaghan equation of state and the experimental unit cell volumes of $\text{Pr}_{1-x}\text{Y}_x\text{Mn}_2\text{Ge}_2$ can be used to derive the related "chemical pressure". It is accepted that the Murnaghan equation can be described [22] as:

$$P(V) = \frac{B_0}{B_0'} \left(\left(\frac{V_0}{V} \right)^{B_0'} - 1 \right) \quad (1)$$

where B_0 is the isothermal bulk modulus, B_0' is its pressure derivative, and V_0 and V are the volumes at ambient pressure and pressure p , respectively. Using the values of $B_0 = 73.5 \text{ GPa}$ and $B_0' = 11.4$ from the closely related compound UMn_2Ge_2 [22], the equivalent "chemical pressure" from $\text{Pr}_{1-x}\text{Y}_x\text{Mn}_2\text{Ge}_2$ compounds can be derived as shown in Figure 1(c). The distinct change in slope which occurs in the calculated chemical pressure around $x=0.5-0.6$ at room temperature (Figure 1(c)), is likely to be related to the change in magnetic state from canted ferromagnetism for $x < \sim 0.6$ to canted antiferromagnetism for $x > \sim 0.6$ (see Figure 5 below). This change in slope is drawn out more clearly in the insert to Figure 1(c) which shows the reduced unit cell volume V/V_0 versus Y concentration for $\text{Pr}_{1-x}\text{Y}_x\text{Mn}_2\text{Ge}_2$ compounds at room temperature (V_0 is the volume of the PrMn_2Ge_2 unit cell while V is the volume for $\text{Pr}_{1-x}\text{Y}_x\text{Mn}_2\text{Ge}_2$ compounds at room temperature). As discussed previously, related RMn_2X_2 compounds exhibit a larger unit cell volume in the Fmc state than in the AFmc state (see e.g. [17] and references therein).

Magnetic Transitions: In considering the magnetic regions for the $\text{Pr}_{1-x}\text{Y}_x\text{Mn}_2\text{Ge}_2$ samples ($x=0.0 - 1.0$), the

Figure 1 (a) Room temperature x-ray diffraction patterns and Rietveld refinements of the $\text{Pr}_{1-x}\text{Y}_x\text{Mn}_2\text{Ge}_2$ compounds ($\text{CuK}\alpha$ radiation); (b) composition dependence of lattice parameters (open symbols taken from reference [21]). The full lines represent linear fits to the present data; the dashed lines indicate the values $a_{\text{crit}1}=4.06$ Å and $a_{\text{crit}2}=4.02$ Å as discussed in the text. (c) The calculated chemical pressure based on the values of $B_0=73.5$ GPa and $B'_0=11.4$ for UMn_2Ge_2 [22] as a function of Y content. The full line is a guide to the eye. The insert shows the composition dependence of the changes in reduced unit cell volume V/V_0

versus Y concentration (V_0 is the volume of the PrMn_2Ge_2 unit cell while V is the volume for $\text{Pr}_{1-x}\text{Y}_x\text{Mn}_2\text{Ge}_2$ compounds at room temperature). The arrow indicates the region where a change in slope is obtained between two linear regions above and below $x \sim 0.6$.

transition temperatures are first identified with their predominant physical influence. In particular with decreasing temperature from the paramagnetic (PM) region: T_N^{intra} defines the magnetic transition from paramagnetism to intralayer antiferromagnetic ordering within the (001) Mn layers (AFI); T_C^{inter} defines the transition from AFI to a canted spin structure (*Fmc*); $T_{c/c}$ defines the transformation temperature of the magnetic structure from *Fmc* to a conical configuration *Fmi* type, T_N^{inter} denotes the change from *Fmc* to the antiferromagnetic canted structure *AFmc* and T_C^{Pr} defines the transition temperature for onset of the ordering of the Pr sublattice [17, 18].

The magnetization and DSC curves for $\text{Pr}_{1-x}\text{Y}_x\text{Mn}_2\text{Ge}_2$ compounds were used to determine the possible magnetic phase transitions. As examples, Figure 2(a) shows the composite magnetization and DSC data over the temperature range ~ 5 -500 K for PrMn_2Ge_2 with Figure 2(b) showing the DSC data for $\text{Pr}_{0.8}\text{Y}_{0.2}\text{Mn}_2\text{Ge}_2$. In the case of the PrMn_2Ge_2 compound, four magnetic phase transitions have been observed in the range 5 K to 500 K. The

Figure 2 (a) Composite figure showing the temperature dependent magnetization obtained on cooling PrMn_2Ge_2 in a field of $B=0.01$ T (5-350 K; left part) and the results of DSC measurements (300-500 K; right part). The transition temperatures are indicated by arrows. (b) The DSC results for the $\text{Pr}_{0.8}\text{Y}_{0.2}\text{Mn}_2\text{Ge}_2$ compound.

transitions, as marked by arrows in Figure 2(a), are indicated as T_C^{Pr} , $T_{C/C}$, T_C^{inter} and T_N^{intra} with increasing temperature. By comparison, only two transitions are detected in the $\text{Pr}_{0.2}\text{Y}_{0.8}\text{Mn}_2\text{Ge}_2$ compound with no transitions occurring below 300 K.

Neutron Diffraction: A set of neutron powder diffraction patterns have been obtained for selected $\text{Pr}_{1-x}\text{Y}_x\text{Mn}_2\text{Ge}_2$ compounds over the temperature range 5-450 K (Figures 3(a) and 3(c)). As noted above, Rietveld refinements were carried out on all patterns using the FULLPROF program package which allows us to derive the structural and magnetic parameters. As explained fully in related articles [14, 17-18], the specific location of Mn atoms on the 4d site in the ThCr_2Si_2 structure (space group $I4/mmm$) allows ready identification of various magnetic structures from key indicators in the neutron diffraction patterns as follows.

- (1) Ferromagnetic ordering of the Mn atoms – hkl reflections with $h + k = 2n$ and $l = 2n$; (e.g. (112) reflections);
- (2) Antiferromagnetic ordering of the Mn atoms within the (001) planes - reflections with $h + k = 2n + 1$; (e.g. (101), (103) reflections);
- (3) Collinear antiferromagnetic structure between adjacent Mn planes - reflections with $h + k + l = 2n + 1$; (e.g. (111), (113) reflections);
- (4) Ferromagnetic mixed incommensurate structure (Fmi) of wave vector $(0, 0, q_z)$ - satellite reflections with $h + k = 2n + 1$; (e.g. (101), (103)).

Figure 3 (a) Neutron diffraction patterns and Rietveld refinements for PrMn_2Ge_2 at 450 K, 350 K, 300 K, 200 K and 10 K ($\lambda=2.4205$ Å). These temperatures were selected as characteristic of the neutron diffraction pattern for each magnetic state. (b) Representative diffraction patterns for $\text{Pr}_{0.5}\text{Y}_{0.5}\text{Mn}_2\text{Ge}_2$ over the temperature range 5-305 K at 10 K intervals ($\lambda=2.4072$ Å). (c) The intensities of the (101), (112) and (200) magnetic peaks as a function of temperature for PrMn_2Ge_2 . The temperature variation of the purely nuclear (002) peak is shown for comparison.

The refinement results for each of the four magnetic states of the PrMn_2Ge_2 compound at selected temperatures (*cf.* transition temperatures in Figure 2(a)) are shown as typical examples in Figure 3(a). It is clear that the neutron diffraction pattern characteristic of each magnetic state, matches well with the intensities expected from magnetic contributions to the neutron scattering as outlined above. The refinement results for PrMn_2Ge_2 at these selected temperatures are listed in Table 1. Figure 3(c) shows the intensities of the (101), (112) and (200) magnetic peaks as a function of temperature with the transitions from the different magnetic phases identified readily from changes in the magnetic scattering. The invariant behaviour of the purely nuclear (002) peak is shown in Figure 3(c) for comparison.

For $\text{Pr}_{0.2}\text{Y}_{0.8}\text{Mn}_2\text{Ge}_2$, the lattice parameter a at room temperature is derived to be $a = 4.020(1)$ Å with $d_{\text{Mn-Mn}} = 2.843$ Å (this $d_{\text{Mn-Mn}}$ spacing is very close to the second

critical value, $d_{Mn-Mn}^{crit2}=2.84$ Å, for occurrence of the AFil structure as mentioned above). Wang *et al.* [21] reported a value of $a=3.996$ Å (smaller than $a_{crit2}=4.02$ Å) for the lattice parameter of YMn_2Ge_2 , Szytula and Szott [23] having earlier shown that YMn_2Ge_2 has the AFil structure. Given the proximity of the a lattice parameter of $Pr_{0.2}Y_{0.8}Mn_2Ge_2$ to the critical value a_{crit2} , we considered two possible magnetic structural models (Figures 4(b) and 4(c)), for refinement of the 300 K neutron diffraction pattern of $Pr_{0.2}Y_{0.8}Mn_2Ge_2$.

The first model is the AFil structure which features a collinear antiferromagnetic structure along the c -axis. The second model is the AFmc structure in which the antiferromagnetic mixed commensurate structure is characterized by antiferromagnetic interplanar coupling of the in-plane ferromagnetic components and by the commensurate ordering of the antiferromagnetic in-plane components. Comparison of the refinements in Figures 4(b) and 4(c) (see inserts for details of the (101) reflection), indicates that at 300 K the AFmc structure provides a significantly improved description of the diffraction data compared with the AFil structure. This description of the AFmc structure for $Pr_{0.2}Y_{0.8}Mn_2Ge_2$ in the temperature region below T_1 (Figure 2(b)) indicates that T_1 can be defined as T_N^{inter} where the AFil layered antiferromagnetic structure transforms to the canted AFmc structure. Correspondingly T_2 can be assigned as T_N^{intra} where the magnetic state changes from paramagnetism (PM) to the AFil antiferromagnetism with decreasing temperature. The refinement for the entire room temperature diffraction pattern of $Pr_{0.2}Y_{0.8}Mn_2Ge_2$ to the AFmc structure is shown in Figure 4(a) with the resultant structural and magnetic parameters shown in Figure 4(d).

Magnetic Phase Diagram: Combining the present findings with the published results [21, 23, 24, 25] has enabled us to construct magnetic phase diagrams for the $Pr_{1-x}Y_xMn_2Ge_2$ system as a function of Y content as in Figure 5 (the phase diagram versus a lattice parameter and intralayer distance d_{Mn-Mn}^a between Mn-Mn within the ab-plane can be seen in reference [26]).

Figure 5 demonstrates that, as expected, the magnetic states at room temperature have been modified by Y substitution due to the contraction of the unit cell. Samples with $x > \sim 0.7$ where the lattice constant a is below $a_{crit1} = 4.06$ Å (Figure 1(b)) are antiferromagnetic at room temperature with no ferromagnetic order evident over the entire temperature range, whereas samples of Y content $x < \sim 0.7$ are ferromagnetic at room temperature. In RMn_2X_2 compounds there are three magnetic interactions (R-R, R-Mn and Mn-Mn) below T_C^R , the temperature at which the rare earth sublattice orders. In $Pr_{1-x}Y_xMn_2Ge_2$ compounds, the R-R and R-Mn magnetic interactions become weaker with increasing Y content due to the dilution effect caused by introduction of the non-magnetic Y atoms. This behaviour is evident, for example, in the decrease of T_C^{Pr}

Figure 4 (a) Neutron diffraction pattern of $Pr_{0.2}Y_{0.8}Mn_2Ge_2$ at 300 K and Rietveld refinement to the AFmc structure; (b) refinement for the AFil model shown over an expanded 2θ range and (c) refinement for the AFmc model over an expanded 2θ range; (d) temperature dependence of lattice parameters and magnetic moment values of $Pr_{0.2}Y_{0.8}Mn_2Ge_2$ as determined from refinements to the AFmc structure.

with increasing Y concentration from $T_C^{Pr} \sim 100$ K for $PrMn_2Ge_2$ to $T_C^{Pr} \sim 0$ K for Y concentration around $x \sim 0.7$ (Figure 5).

Figure 5 Magnetic phase diagram of $\text{Pr}_{1-x}\text{Y}_x\text{Mn}_2\text{Ge}_2$ as a function of the Y content (closed symbols - present results; open symbols - data from [21, 23, 24, 25]). As discussed in the text, T_N^{intra} (squares) defines the transition from paramagnetism to intralayer antiferromagnetic ordering within the (001) Mn layers (AFi); T_C^{inter} (circles) defines the transition from AFi to a canted spin structure (Fmc); $T_{c/c}$ (inverted triangle) defines the transformation temperature of the magnetic structure from Fmc to a conical configuration Fmi type, T_N^{inter} (triangle) denotes the transition to the antiferromagnetic canted structure AFmc and T_C^{Pr} (stars) defines the transition temperature for onset of the ordering of the Pr sublattice. The dashed lines indicate trends in the data. As discussed in the text, the vertical dashed line located around Y concentration of $x \sim 0.86$ is used as a tentative guide to the boundary between the AFmc and AFil regions.

As is clear from the phase diagram in Figure 5, $\text{Pr}_{1-x}\text{Y}_x\text{Mn}_2\text{Ge}_2$ compounds with Y content $x > 0.7$ show a relatively simple magnetic behaviour, transforming from paramagnetism at high temperature to AFi followed by AFmc with decreasing temperature with no evidence of paramagnetism at high temperature to AFi followed by AFmc with decreasing temperature with no evidence of ordering of the Pr-sublattice. As noted above, YMn_2Ge_2 exhibits the layered AFil structure although the boundary between the AFmc and AFil magnetic structures at high Y contents has yet to be delineated. It is assumed that the boundary between the AFmc and AFil regions originates around the paramagnetic transition for these phases at Y concentration $x = \sim 0.86$. By comparison, Pr-rich samples ($x < 0.4$) successively exhibit four magnetic states – AFi, Fmc, Fmi, Fmi+F(Pr) – on cooling from the high temperature paramagnetic phase, while re-entrant ferromagnetism has been observed for compounds with Y contents in the range $x \sim 0.4$ – 0.6 . Figure 5 also indicates that the Fmi structure only occurs for Y content $x < \sim 0.4$.

This is reflected by the decrease in wave vector with Y content from $q_c = 0.272$ for PrMn_2Ge_2 at 10 K to $q_c = 0.237$ for $\text{Pr}_{0.8}\text{Y}_{0.2}\text{Mn}_2\text{Ge}_2$ at 10 K. Similar behaviour has

Table 1 Rietveld refinement results for PrMn_2Ge_2 at 10 K, 200 K, 300 K, 350 K and 450 K. These temperatures were selected as characteristic of the neutron diffraction pattern of each magnetic state (cf. Figure 3(a)). The standard errors derived from the refinements are also listed.

T (K)	10 K	200 K	300 K	350 K	450 K
Magnetic state	$Fmi+F(Pr)$	Fmi	Fmc	AFi	PM
a (Å)	4.107(1)	4.114(1)	4.119(1)	4.121(1)	4.126(1)
c (Å)	10.881(1)	10.891(1)	10.905(2)	10.919(2)	10.951(2)
z_{Ge}	0.3820(2)	0.3827(2)	0.3825(2)	0.3826(2)	0.3826(2)
$\mu_{\text{ab}}(\mu_B)$	2.51(4)	2.33(4)	2.08(3)	1.86(3)	-
$\mu_c(\mu_B)$	2.03(5)	1.95(5)	1.28(6)	-	-
canting angle (°)	51.0(9)	53.6(8)	58.4(6)	90	-
$\mu_{\text{tot}}(\mu_B)$	3.23(7)	2.90(4)	2.44(5)	1.86(3)	--
q_c	0.272(2)	0.214(1)	-	-	-
$\mu_{\text{Pr}}(\mu_B)$	1.53(3)	-	-	-	-

been detected in the $\text{PrMn}_{2-x}\text{Fe}_x\text{Ge}_2$ [14] and $\text{Pr}_{1-y}\text{Lu}_y\text{Mn}_2\text{Ge}_2$ [27] systems where the absence of the Fmi structure is noted for $x < 0.38$ and $y < 0.4$, respectively.

Given that the magnetic structure in RMn_2Ge_2 and related systems depends sensitively on the intraplanar Mn-Mn spacing and that both external pressure and the substitution of Y for Pr in $\text{Pr}_{1-x}\text{Y}_x\text{Mn}_2\text{Ge}_2$ can reduce the Mn-Mn distance, it is interesting to compare the relative impact of chemical pressure and applied pressure on the magnetic order. Here we consider the variation of T_N^{inter} with Y content (considered here as equivalent to effects of chemical pressure) and external pressure as detected in $\text{Pr}_{0.5}\text{Y}_{0.5}\text{Mn}_2\text{Ge}_2$ [18], where we made such a comparison for T_C^{Pr} . As is evident from Figure 5, these two transitions were chosen because of their higher sensitivity to the composition change (and Mn-Mn distance [26]).

With increase in Y content, T_N^{inter} , the transition from the canted Fmc magnetic structure to the canted AFmc magnetic structure, increases from ~ 200 K for $x=0.4$ to ~ 373 K for $x=0.8$ (Figure 5). The corresponding chemical pressure changes from ~ 12.6 kbar for $x=0.4$ to ~ 50.7 kbar for $x=0.8$, leading to a rate of change $dT_N^{\text{inter}}/dp = 4.5$ K/kbar compared with the rate of change in transition temperature with external pressure of $dT_N^{\text{inter}}/dp = 22.2$ K/kbar in $\text{Pr}_{0.5}\text{Y}_{0.5}\text{Mn}_2\text{Ge}_2$ [18]. Estimation of the value of chemical pressure due to Y substitution for Pr using the isothermal bulk modulus B_0 and its pressure derivative B_0' of UMn_2Ge_2 [22] is expected to include additional uncertainty because the magnetic states change with pressure from Fmc to AFmc (see [26]) and different magnetic states are expected to have different B_0 and B_0' . Given this additional uncertainty, we think the comparison for dT_N^{inter}/dp is consistent with change in T_C^{Pr} , as discussed in [18] where we noted the rate of change with mechanical pressure exceeds the change with chemical pressure by a factor of ~ 2 . Comparison of the effects of chemical pressure and applied pressure demonstrates that while the Y substitution for Pr produces changes consistent

with the effect of pressure, additional effects occur. These effects are associated with the differences in the electron configurations of Pr^{3+} ($4f^2$) and Y^{3+} ($4d^0$) ions with electronic effects likely to explain the different rates of change for both dT_C^{Pr}/dp and dT_N^{inter}/dp for chemical pressure and external pressure.

Magnetocaloric Effect: We have calculated the magnetocaloric effect around T_C^{inter} for the set of samples from magnetization data using the standard Maxwell thermodynamic relation [e.g. 28]. The magnetization results for PrMn_2Ge_2 in the region of $T_C^{\text{inter}} \sim 334$ K are shown as an example in Figure 6(a) with the corresponding Arrott plots of M^2 versus B/M presented in Figure 6(b). The positive intercepts of the linear extrapolation of the magnetisation data with the M^2 axis below T_C^{inter} (determined from the temperature of zero intercept in Figure 6(b)), demonstrates the ferromagnetic nature of the magnetic phase below T_C^{inter} . The positive slopes of the Arrott plots around T_C^{inter} indicate that the magnetic transition at T_C^{inter} for PrMn_2Ge_2 is second order. Similarly, analyses of the Arrott-plots for $\text{Pr}_{0.8}\text{Y}_{0.2}\text{Mn}_2\text{Ge}_2$ and $\text{Pr}_{0.5}\text{Y}_{0.5}\text{Mn}_2\text{Ge}_2$ demonstrate that the ferromagnetic transitions at T_C^{inter} for these compounds are also second order.

Figure 6 (a) Magnetisation versus field curves ($B = 0-5$ T) for PrMn_2Ge_2 over the temperature region around $T_C^{\text{inter}} \sim 334$ K; (b) the corresponding Arrott plots of M^2 versus B/M for PrMn_2Ge_2 .

The isothermal magnetic entropy change, $-\Delta S_M$, for the PrMn_2Ge_2 and $\text{Pr}_{0.8}\text{Y}_{0.2}\text{Mn}_2\text{Ge}_2$ samples are shown as a function of temperature in Figures 7(a) and 7(b) respectively. The maximum entropy values $-\Delta S_M$ around the ferromagnetic transition temperature T_C^{inter} for the $\text{Pr}_{1-x}\text{Y}_x\text{Mn}_2\text{Ge}_2$ compounds with $x=0.0, 0.2$ and 0.5 have been derived to be 3.0 J/kg K, 2.94 J/kg K and 3.47 J/kg K respectively (field change $\Delta B=0.5$ T). Compared with other rare earth intermetallic compounds which also exhibit a second order phase transition around room temperature, the present set of $\text{Pr}_{1-x}\text{Y}_x\text{Mn}_2\text{Ge}_2$ compounds exhibit moderate isothermal magnetic entropy. As examples, the values of $-\Delta S_M$ for $\text{Ho}_2\text{Fe}_{17-x}\text{Mn}_x$ are 3.2 J $\text{kg}^{-1}\text{K}^{-1}$ around $T_C=336$ K ($x=0.0$) and 2.7 J $\text{kg}^{-1}\text{K}^{-1}$ around $T_C=302$ K ($x=2.0$) respectively [29]. $\text{Er}_2\text{Fe}_{17}$ has recently been found to exhibit similar entropy value of $-\Delta S_M=3.6$ J $\text{kg}^{-1}\text{K}^{-1}$ around 300 K for $\Delta B = 0.5$ T [30]. The present set of entropy values are similar to those obtained for related compounds in the RMn_2X_2 series which also exhibit magnetic transitions around ~ 330 K. Dincer and Elerman [31] obtained maximum entropy values in the approximate range $-\Delta S_M \sim 2-3$ J $\text{kg}^{-1}\text{K}^{-1}$ ($\Delta B=0.5$ T) around the paramagnetic to ferromagnetic Curie temperatures $T_C \sim 300-320$ K for re-entrant $\text{SmMn}_{2-x}\text{Fe}_x\text{Ge}_2$ ($x = 0.05, 0.10$) and $\text{SmMn}_{2-x}\text{Co}_x\text{Ge}_2$ ($x = 0.05, 0.15$) compounds. On the other hand a reduced entropy value of $-\Delta S_M \sim 1.8$ J $\text{kg}^{-1}\text{K}^{-1}$ was obtained for a $\text{Pr}_{0.1}\text{Gd}_{0.9}\text{Mn}_2\text{Ge}_2$ sample around the antiferromagnetic to ferromagnetic Curie temperature $T_C \sim 340$ K [32].

It is well accepted that the following relationship applies for a magnetic system with a second-order phase transition [33, 34]:

$$|\Delta S_M^{\text{PK}}| \propto B^{2/3} \quad (2)$$

where $-\Delta S_M^{\text{PK}}$ is the peak value of the magnetic entropy change at different magnetic fields B . It can be seen from Figure 7(c) that this relationship is valid for the $\text{Pr}_{1-x}\text{Y}_x\text{Mn}_2\text{Ge}_2$ compounds with $x=0.0, 0.2$ and 0.5 around T_C^{inter} . This agreement of $-\Delta S_M^{\text{PK}}$ with relationship (2) confirms the second order nature of these transitions as demonstrated by the Arrott plot analyses and discussed above (e.g. Figure 6(b) for PrMn_2Ge_2).

4 Conclusions

Replacement of Y for Pr leads to a significant reduction in the lattice parameter of $\text{Pr}_{1-x}\text{Y}_x\text{Mn}_2\text{Ge}_2$ compounds. The commensurate changes in the intralayer Mn–Mn distances correspondingly lead to a variety of magnetic structures, as also observed in related RMn_2X_2 systems (R – rare earth; X – Ge, Si) [e.g. 35, 36]. We have determined the various magnetic structures of $\text{Pr}_{1-x}\text{Y}_x\text{Mn}_2\text{Ge}_2$ by neutron powder diffraction over the temperature range $5 - 450$ K. Together with magnetisation and differential scanning calorimetry measurements, this has enabled us to construct the

magnetic phase diagram of $\text{Pr}_{1-x}\text{Y}_x\text{Mn}_2\text{Ge}_2$. The ferromagnetic transitions at T_C^{inter} , the temperature at which the layered antiferromagnetic structure transforms to the canted Fmc structure, are found to be second order. The entropy changes around T_C^{inter} have been derived for $\text{Pr}_{1-x}\text{Y}_x\text{Mn}_2\text{Ge}_2$ compounds of Y contents $x = 0.0, 0.2$ and 0.5 .

Figure 7 Temperature dependence of the isothermal magnetic entropy change $-\Delta S_M$ for: (a) PrMn_2Ge_2 and (b) $\text{Pr}_{0.8}\text{Y}_{0.2}\text{Mn}_2\text{Ge}_2$. (c) Dependence of $-\Delta S_M^{\text{PK}}$ (peak value of the magnetic entropy change at different B) on the parameter $B^{2/3}$ for $\text{Pr}_{1-x}\text{Y}_x\text{Mn}_2\text{Ge}_2$ compounds with $x=0.0, 0.2$ and 0.5 . The linear fits to the data as shown by the dashed lines are discussed in the text.

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