Magnetic transitions and the magnetocaloric effect in the Pr 1-xYxMn2Ge2 system

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Abstract
Layered rare earth compounds in the RMn2X2 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 Pr1−xYxMn2Ge2 magnetic phase diagram as functions of both composition and Mn-Mn spacing using X-ray and neutron diffraction, magnetization and differential scanning calorimetry measurements. Pr1−xYxMn2Ge2 exhibits an extended region of re-entrant ferromagnetism around x ∼ 0.5 with re-entrant ferromagnetism at inline image for Pr0.5Y0.5Mn2Ge2. The entropy values −ΔSM around the ferromagnetic transition temperatures inline image from the layered antiferromagnetic AFL structure to the canted ferromagnetic structure Fmc (typically inline image) have been derived for Pr1−xYxMn2Ge2 with x = 0.0, 0.2, and 0.5 for ΔB = 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, xyxmn2ge2

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

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Keywords Magnetocaloric effect, magnetic structure, neutron diffraction; Pr$_{1-x}$Y$_x$Mn$_2$Ge$_2$ phase diagram

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Layered rare earth compounds in the RMn$_2$X$_2$ series (R=rare-earth; X=Ge, Si) are of interest for potential cooling applications at lower temperatures as they enable the structural and magnetic behaviour to be controlled via substitution of R, Mn, X atoms on the 2a, 4d and 4e sites respectively. We continue investigations of the Pr$_{1-x}$Y$_x$Mn$_2$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. Pr$_{1-x}$Y$_x$Mn$_2$Ge$_2$ exhibits an extended region of re-entrant ferromagnetism around $x\sim0.5$ with re-entrant ferromagnetism at $T_c^{Pr} \sim 50$ K for Pr$_{0.5}$Y$_{0.5}$Mn$_2$Ge$_2$. The entropy values $\Delta S_M$ around the ferromagnetic transition temperatures $T_c^{inter}$ from the layered antiferromagnetic AF$_l$ structure to the canted ferromagnetic structure F$_mc$ (typically $T_c^{inter} \sim 330-340$ K) have been derived for Pr$_{1-x}$Y$_x$Mn$_2$Ge$_2$ 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.

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 20$^{th}$ Century. A further major development occurred in 1997 with the report of a giant magnetocaloric effect (MCE) near room temperature for Ni$_2$MnGa [6]. This discovery, combined with the environmental impervious 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 magnetostuctural transitions around room temperature [e.g. 11, 12, 13]. Layered rare earth compounds in the RMn$_2$X$_2$ series (R=rare-earth; X=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$_2$Ge$_2$ compounds is strongly influenced by two critical values of the intralayer Mn–Mn distance $d_{Mn-Mn}^{int}$: $d_{int1}$ = 2.87 Å (of related lattice parameter $a_{int1}=4.06$ Å) and $d_{int2}$ = 2.84 Å (related lattice parameter $a_{int2}=4.02$ Å) [14, 17-
18]. For compounds with $d_{\text{inplane}}(\text{Mn-Mn}) > d_{\text{cutoff}}$, the intralayer in-plane coupling is antiferromagnetic and the interlayer coupling is ferromagnetic [14, 17-18] leading to the Fm-type magnetic configuration.

In the case of the Pr$_{1-x}$Y$_x$Mn$_2$Ge$_2$ system, given that PrMn$_2$Ge$_2$ is ferromagnetic and YMn$_2$Ge$_2$ antiferromagnetic at room temperature, the Pr$_{1-x}$Y$_x$Mn$_2$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 Pr$_{1-x}$Y$_x$Mn$_2$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 Pr$_{1-x}$Y$_x$Mn$_2$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 Pr$_{1-x}$Y$_x$Mn$_2$Ge$_2$ compounds (with $x=0.0 - 1.0$) were prepared using conventional argon arc melting. The starting materials contained ~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 (Cu K$_\alpha$ radiation, $\lambda = 1.5418$ Å). The temperature dependences of the DC magnetisation was derived 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 Pr$_{1-x}$Y$_x$Mn$_2$Ge$_2$ (Figure 1(a)) indicates that all of the samples are single phase with the expected body-centred tetragonal ThCr$_2$Si$_2$-type structure (space group 14/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: $da/dx = -0.133$ Å and $dc/dx = -0.053$ Å respectively in accord with Vegard’s Law.

With respect to PrMn$_2$Ge$_2$ 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 pressure dependence of the experimental unit cell volumes of Pr$_{1-x}$Y$_x$Mn$_2$Ge$_2$ can be used to derive the related “chemical pressure”. It is accepted that the Murnaghan equation can be described [22] as:

$$P(V) = \frac{B_o'}{B_o} \left( \frac{V_o}{V} \right)^{\frac{B_o'}{B_o}} - 1$$

where $B_o$ is the isothermal bulk modulus, $B_o'$ is its pressure derivative, and $V_o$ and $V$ are the volumes at ambient pressure and pressure $p$, respectively. Using the values of $B_o = 73.5$ GPa and $B_o' = 11.4$ from the closely related compound UMn$_2$Ge$_2$ [22], the equivalent “chemical pressure” from Pr$_{1-x}$Y$_x$Mn$_2$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 $x = 0.4$-0.6 at room temperature (Figure 1(c)), is likely to be related to the change in magnetic state from antiferromagnetic to ferromagnetic for $x < 0.6$ to canted antiferromagnetism for $x > 0.6$ (see Figure 5 below). This change in slope is drawn out more clearly in the insert to 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 antiferromagnetic to ferromagnetic for $x < 0.6$ to canted antiferromagnetism for $x > 0.6$ (see Figure 5 below). This change in slope is drawn out more clearly in the insert to 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 antiferromagnetic to ferromagnetic for $x < 0.6$ to canted antiferromagnetism for $x > 0.6$ (see Figure 5 below). This change in slope is drawn out more clearly in the insert to Figure 1(c).
transition temperatures are first identified with their predominant physical influence. In particular with decreasing temperature from the paramagnetic (PM) region: \( T_{N\text{ intra}} \) defines the magnetic transition from paramagnetism to intralayer antiferromagnetic ordering within the (001) Mn layers (AFI); \( T_{C\text{ inter}} \) defines the transition from AFI to a canted spin structure (Fmc); \( T_{C\text{ intra}} \) defines the transformation temperature of the magnetic structure from Fmc to a conical configuration Fml type, \( T_{N\text{ intra}} \) denotes the change from Fmc to the antiferromagnetic canted structure AFmc and \( T_{C\text{ Pr}} \) defines the transition temperature for onset of the ordering of the Pr sublattice [17, 18].

The magnetization and DSC curves for \( Pr_{1-x}Y_xMn_2Ge_2 \) 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 \( \sim 5-500 \) K for \( PrMn_2Ge_2 \) with Figure 2(b) showing the DSC data for \( Pr_{0.8}Y_{0.2}Mn_2Ge_2 \). 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


transitions, as marked by arrows in Figure 2(a), are indicated as \( T_{C_n}^{Pr}, T_{C_{in}}^{Pr}, T_{C_{in}}^{int} \) and \( T_{N}^{intra} \) with increasing temperature. By comparison, only two transitions are detected in the \( Pr_{0.2}Y_{0.8}Mn_2Ge_2 \) compound with no transitions occurring below 300 K.

**Neutron Diffraction:** A set of neutron powder diffraction patterns have been obtained for selected \( Pr_{1-x}Y_xMn_2Ge_2 \) 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](image_url)

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 \( Pr_{0.5}Y_{0.5}Mn_2Ge_2 \) 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 \( Pr_{0.2}Y_{0.8}Mn_2Ge_2 \), the lattice parameter \( a \) at room temperature is derived to be \( a = 4.020(1) \) Å with \( d_{Mn-Mn} = 2.843 \) Å (this \( d_{Mn-Mn} \) spacing is very close to the second
critical value, $a_{\text{crit 1}} = 3.84$ Å, for occurrence of the AFil structure as mentioned above). Wang et al. [21] reported a value of $a = 3.996$ Å (smaller than $a_{\text{crit 2}} = 4.02$ Å) for the lattice parameter of YMn$_2$Ge$_2$, Szytula and Szott [23] having earlier shown that YMn$_2$Ge$_2$ has the AFil structure. Given the proximity of the $a$ lattice parameter of Pr$_{0.2}$Y$_{0.8}$Mn$_2$Ge$_2$ to the critical value $a_{\text{crit 2}}$, 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$_2$Ge$_2$.

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$_2$Ge$_2$ in the temperature region below $T_1$ (Figure 2(b)) indicates that $T_1$ can be defined as $T_N^{\text{inter}}$ where the AFil layered antiferromagnetic structure transforms to the canted AFmc structure. Correspondingly $T_2$ can be assigned as $T_N^{\text{intra}}$ where the magnetic state changes from paramagnetism (PM) to the AFi antiferromagnetism with decreasing temperature. The refinement for the entire room temperature diffraction pattern of Pr$_{0.2}$Y$_{0.8}$Mn$_2$Ge$_2$ 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$_x$Mn$_2$Ge$_2$ system as a function of Y content as in Figure 5 (the phase diagram versus $a$ lattice parameter and intralayer distance $d_{\text{Mn-Mn}}$ 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 $x > 0.7$ where the lattice constant $a$ is below $a_{\text{crit 1}} = 4.06$ Å (Figure 1(b)) are antiferromagnetic at room temperature with no ferromagnetic order evident over the entire temperature range, whereas samples of Y content $x < 0.7$ are ferromagnetic at room temperature. In RMn$_2$X$_2$ compounds there are three magnetic interactions (R-R, R-Mn and Mn-Mn) below $T_C$, the temperature at which the rare earth sublattice orders. In Pr$_{1-x}$Y$_x$Mn$_2$Ge$_2$ 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 $T_{C_{\text{Pr}}}$ with increasing Y concentration from $T_{C_{\text{Pr}}} \sim 100$ K for PrMn$_2$Ge$_2$ to $T_{C_{\text{Pr}}} \sim 0$ K for Y concentration around $x \sim 0.7$ (Figure 5).
As is clear from the phase diagram in Figure 5, Pr$_{1-x}$Y$_x$Mn$_2$Ge$_2$ compounds with Y content $x > 0.7$ show a relatively simple magnetic behaviour, transforming from paramagnetism at high temperature to AFmc followed by AFmc with decreasing temperature with no evidence of ordering of the Pr sublattice. It is assumed that the boundary between the AFmc and AFil magnetic structures at high Y contents has yet to be delineated. It is 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 – AFl, 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 $x < 0.4$.

This is reflected by the decrease in wave vector with Y content from $q_e = 0.272$ for PrMn$_2$Ge$_2$ at 10 K to $q_e = 0.237$ for Pr$_{0.8}$Y$_{0.2}$Mn$_2$Ge$_2$ at 10 K. Similar behaviour has been observed in the PrMn$_2$Fe$_2$Ge$_2$ [14] and Pr$_{1-x}$Lu$_x$Mn$_2$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$_2$Ge$_2$ and related systems depends sensitively on the intraplanar Mn-Mn spacing and that both external pressure and the substitution of Y for Pr in Pr$_{1-x}$Y$_x$Mn$_2$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 $T_{N\text{inter}}$ with Y content (considered here as equivalent to effects of chemical pressure) and external pressure as detected in Pr$_{0.5}$Y$_{0.5}$Mn$_2$Ge$_2$ [18], where we made such a comparison for $T_{C\text{Pr}}$. 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, $T_{N\text{inter}}$, 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 $dT_N/dp = 4.5$ 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 Pr$_{0.5}$Y$_{0.5}$Mn$_2$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$_2$Ge$_2$ [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 $dT_N\text{inter}/dp$ is consistent with change in $T_{C\text{Pr}}$, as discussed in [18] where we noted the rate of change of magnetic 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

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**Table 1** Rietveld refinement results for PrMn$_2$Ge$_2$ 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.

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**Figure 5** Magnetic phase diagram of Pr$_{1-x}$Y$_x$Mn$_2$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, $T_{N\text{inter}}$ (squares) defines the transition from paramagnetism to intralayer antiferromagnetic ordering within the (001) Mn layers (AFi); $T_{N\text{inter}}$ (circles) defines the transition from AFi to a canted spin structure (Fmc); $T_{C\text{Pr}}$ (inverted triangle) defines the transformation temperature of the magnetic structure from Fmc to a conical configuration PM type, $T_{N\text{inter}}$ (triangle) denotes the transition to the antiferromagnetic canted structure AFmc and $T_{C\text{Pr}}$ (stars) defines the transformation 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.
with the effect of pressure, additional effects occur. These effects are associated with the differences in the electron configurations of Pr$^{3+}$ (4f$^0$) and Y$^{3+}$ (4d$^0$) ions with electronic effects likely to explain the different rates of change for both $dT_C^\text{inter}$ and $dT_N^\text{inter}/dp$ for chemical pressure and external pressure.

**Magnetocaloric Effect:** We have calculated the magnetocaloric effect around $T_C$ for the set of samples from magnetization data using the standard Maxwell thermodynamic relation [e.g. 28]. The magnetization results for PrMn$_2$Ge$_2$ in the region of $T_C^\text{inter}$ ~ 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 $T_C^\text{inter}$ (determined from the temperature of zero intercept in Figure 6(b)), demonstrates the ferromagnetic nature of the magnetic phase below $T_C^\text{inter}$. The positive slopes of the Arrott plots around $T_C^\text{inter}$ indicate that the magnetic transition at $T_C^\text{inter}$ for PrMn$_2$Ge$_2$ is second order. Similarly, analyses of the Arrott-plots for $Pr_{1-x}Y_xMn_2Ge_2$ and $Pr_{0.5}Y_{0.5}Mn_2Ge_2$ demonstrate that the ferromagnetic transitions at $T_C^\text{inter}$ for these compounds are also second order.

The isothermal magnetic entropy change, $-\Delta S_M$ for the Pr$_{1-x}Y_xMn_2Ge_2$ and Pr$_{0.5}Y_{0.5}Mn_2Ge_2$ 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 $T_C^\text{inter}$ for the Pr$_{1-x}Y_xMn_2Ge_2$ 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 $Pr_{1-x}Y_xMn_2Ge_2$ compounds exhibit moderate isothermal magnetic entropy.

As examples, the values of $-\Delta S_M$ for Ho$_2$Fe$_{17}$, $Mn_2$ are 3.2 J kg$^{-1}$K$^{-1}$ around $T_C=336$ K ($x=0.0$) and 2.7 J kg$^{-1}$K$^{-1}$ around $T_C=302$ K ($x=2.0$) respectively [29]. Er$_2$Fe$_{17}$ has recently been found to exhibit similar entropy value of $-\Delta S_M=3.6$ J kg$^{-1}$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$_2$X$_2$ series which also exhibit magnetic transitions around ~330 K. Dincer and Elerman [31] obtained maximum entropy values in the approximate range $-\Delta S_M=2$-3 J kg$^{-1}$K$^{-1}$ ($\Delta B=0$-5 T) around the paramagnetic to ferromagnetic Curie temperatures $T_C=300$-320 K for re-entrant SmMn$_2$Fe$_2$Ge$_2$ ($x=0.05, 0.10$) and SmMn$_2$Co$_{0.5}$Ge$_2$ ($x=0.05, 0.15$) compounds. The other hand a reduced entropy value of $-\Delta S_M=1.8$ J kg$^{-1}$K$^{-1}$ was obtained for a Pr$_{0.1}$Gd$_{0.9}$Mn$_2$Ge$_2$ sample around the antiferromagnetic to ferromagnetic Curie temperature $T_C=340$ K [32].

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

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

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 $Pr_{1-x}Y_xMn_2Ge_2$ compounds with $x=0.0, 0.2$ and 0.5 around $T_C^\text{inter}$. 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$_2$Ge$_2$).

**4 Conclusions**

Replacement of Y for Pr leads to a significant reduction in the lattice parameter of $Pr_{1-x}Y_xMn_2Ge_2$ compounds. The commensurate changes in the intralayer Mn–Mn distances correspondingly lead to a variety of magnetic structures, as also observed in related RMn$_2$X$_2$ systems (R – rare earth; X - Ge, Si) [e.g. 35, 36]. We have determined the various magnetic structures of $Pr_{1-x}Y_xMn_2Ge_2$ 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 Pr$_{1-x}$Y$_x$Mn$_2$Ge$_2$. The ferromagnetic transitions at $T_{\text{C,inter}}$, the temperature at which the layered antiferromagnetic structure transforms to the canted Fmc structure, are found to be second order. The entropy changes around $T_{\text{C,inter}}$ have been derived for Pr$_{1-x}$Y$_x$Mn$_2$Ge$_2$ compounds of Y contents $x = 0.0$, 0.2 and 0.5.

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