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

Jianli Wang  
*University of Wollongong*, jianli@uow.edu.au

S J. Campbell  
*University of New South Wales*, stewart.campbell@adfa.edu.au

M F. Md Din  
*University of Wollongong*, mfmd999@uowmail.edu.au

S J. Kennedy  
*ANSTO*

M Hofmann  
*Technische Universitat Munchen*

Follow this and additional works at: https://ro.uow.edu.au/aiimpapers

Part of the Engineering Commons, and the Physical Sciences and Mathematics Commons

**Recommended Citation**

Wang, Jianli; Campbell, S J.; Md Din, M F.; Kennedy, S J.; and Hofmann, M, "Magnetic transitions and the magnetocaloric effect in the Pr $1-x$Y$_x$Mn$_2$Ge$_2$ system" (2014). *Australian Institute for Innovative Materials - Papers*. 1083.  
https://ro.uow.edu.au/aiimpapers/1083

Research Online is the open access institutional repository for the University of Wollongong. For further information contact the UOW Library: research-pubs@uow.edu.au
Magnetic transitions and the magnetocaloric effect in the Pr $1-x$Y$x$Mn$_2$Ge$_2$ system

Abstract
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 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$_x$Mn$_2$Ge$_2$ 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$_x$Mn$_2$Ge$_2$ exhibits an extended region of re-entrant ferromagnetism around $x \sim 0.5$ with re-entrant ferromagnetism at $\Delta B = 0-5$ T. The entropy values $\Delta SM$ around the ferromagnetic transition temperatures 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.

Keywords
transitions, magnetocaloric, effect, pr, magnetic, 1, system, xyxmn2ge2

Disciplines
Engineering | Physical Sciences and Mathematics

Publication Details

This journal article is available at Research Online: https://ro.uow.edu.au/aiimpapers/1083
Magnetic transitions and the magnetocaloric effect in the 
Pr$_{1-x}$Y$_x$Mn$_2$Ge$_2$ system

J. L. Wang$^{1,2,3}$, S. J. Campbell$^1$, * M. F. Md Din$^2$, S. J. Kennedy$^3$ and M. Hofmann$^4$

$^1$ School of Physical, Environmental and Mathematical Sciences, University of New South Wales, Canberra, ACT 2600, Australia
$^2$ Institute for Superconductivity and Electronic Materials, University of Wollongong, Wollongong, NSW 2522, Australia
$^3$ Bragg Institute, Australian Nuclear Science and Technology, Lucas Heights, NSW 2234, Australia
$^4$ Forschungs-Neutronequelle Heinz Maier-Leibnitz (FRM-II), Technische Universität München, Garching 85747, Germany

Received ZZZ, revised ZZZ, accepted ZZZ
Published online ZZZ                 (Dates will be provided by the publisher.)

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

* Corresponding author: stewart.campbell@adfa.edu.au

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~0.5 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 20th Century. 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 [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$_2$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 $d_{Mn-Mn}^1$: $d_{Mn-Mn}^{1_{1,1}} = 2.87$ Å (of related lattice parameter $a_{1,1}=4.06$ Å) and $d_{Mn-Mn}^{1_{2,2}} = 2.84$ Å (related lattice parameter $a_{2,2}=4.02$ Å) [14, 17-19].
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 shows the reduced unit cell volume V/V$_0$ versus Y concentration for Pr$_{1-x}$Y$_x$Mn$_2$Ge$_2$ compounds at room temperature. As discussed previously, related RMn$_2$X$_2$ compounds exhibit a larger unit cell volume in the Fme state than in the AFme state (see e.g. [17] and references therein).

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

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

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 $B_0 = 73.5$ GPa and $B_0' = 11.4$ 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=0.5-0.6 at room temperature (Figure 1(c)), is likely to be related to the change in magnetic state from canted ferromagnetism for x <~ 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) which shows the reduced unit cell volume V/V$_0$ versus Y concentration for Pr$_{1-x}$Y$_x$Mn$_2$Ge$_2$ compounds at room temperature ($V_0$ is the volume of the PrMn$_2$Ge$_2$ unit cell while $V$ is the volume for Pr$_{1-x}$Y$_x$Mn$_2$Ge$_2$ compounds at room temperature). As discussed previously, related RMn$_2$X$_2$ compounds exhibit a larger unit cell volume in the Fme state than in the AFme state (see e.g. [17] and references therein).
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); $T_{C,\text{intra}}$ defines the transition from AFI to a canted spin structure ($Fmc$); $T_{C,\text{c}}$ defines the transformation temperature of the magnetic structure from $Fmc$ to a conical configuration $Fmi$ type; $T_{V,\text{intra}}$ 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$_x$Mn$_2$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$_2$Ge$_2$ with Figure 2(b) showing the DSC data for Pr$_{0.8}$Y$_{0.2}$Mn$_2$Ge$_2$. In the case of the PrMn$_2$Ge$_2$ compound, four magnetic phase transitions have been observed in the range 5 K to 500 K. The

![Figure 1](image1.png)

**Figure 1** (a) Room temperature x-ray diffraction patterns and Rietveld refinements of the Pr$_{1-x}$Y$_x$Mn$_2$Ge$_2$ compounds (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 $a_{\text{intra}}=4.06$ Å and $a_{\text{c}}=4.02$ 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$_2$Ge$_2$ [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$_2$Ge$_2$ unit cell while $V$ is the volume for Pr$_{1-x}$Y$_x$Mn$_2$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 $x \sim 0.6$. 

![Figure 2](image2.png)

**Figure 2** (a) Composite figure showing the temperature dependent magnetization obtained on cooling PrMn$_2$Ge$_2$ 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 Pr$_{0.8}$Y$_{0.2}$Mn$_2$Ge$_2$ compound.
transitions, as marked by arrows in Figure 2(a), are indicated as $T_{C, Pr}^c$, $T_{C, Mn}$, $T_{C, intra}$ and $T_{C, intra}$ with increasing temperature. By comparison, only two transitions are detected in the Pr$_{0.2}$Y$_{0.8}$Mn$_2$Ge$_2$ 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$_x$Mn$_2$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$_2$Si$_2$ 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)).

The refinement results for each of the four magnetic states of the PrMn$_2$Ge$_2$ 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$_2$Ge$_2$ 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 for PrMn$_2$Ge$_2$. The temperature variation of the purely nuclear (002) peak is shown for comparison.

For Pr$_{0.2}$Y$_{0.8}$Mn$_2$Ge$_2$, 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, \( \phi_{Mn-Mn}^{\text{crit}} = 2.84 \text{ Å} \), for occurrence of the AFil structure as mentioned above). Wang et al. [21] reported a value of \( a = 3.996 \text{ Å} \) (smaller than \( a_{\text{cr1}} = 4.02 \text{ Å} \)) 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 \( Pr_{0.2}Y_{0.8}Mn_2Ge_2 \) to the critical value \( a_{\text{cr1}} \), 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 \( T_1 \) where the AFI layered antiferromagnetic structure transforms to the canted AFmc structure. Correspondingly \( T_2 \) can be assigned as \( T_2 \) 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 \( Pr_{0.2}Y_{0.8}Mn_2Ge_2 \) 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 \( d_{\text{Mn-Mn}} \) 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 \( x > \sim 0.7 \) where the lattice constant \( a \) is below \( a_{\text{cr1}} = 4.06 \text{ Å} \) (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\(_2\)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 \( Pr_{1-x}Y_xMn_2Ge_2 \) 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 \( T_C \) with increasing \( Y \) concentration from \( Pr_0Y_{1.0}Mn_2Ge_2 \) at \( 300 \text{ K} \) and Rietveld refinement to the AFmc structure; (b) refinement for the AFil model shown over an expanded \( 2\theta \) range and (c) refinement for the AFmc model over an expanded \( 2\theta \) 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.
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 AFl followed by AFmc with decreasing temperature with no evidence of paramagnetism at high temperature to AFl followed by relatively simple magnetic behaviour, transforming from the antiferromagnetic canted structure AFmc to the canted AF$_{il}$ structure (F$_{mc}$) above the temperature of the magnetic structure from Fmc to a conical configuration Fmi type, $T_{N}^{\text{inter}}$ (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 AF$_{il}$ regions.

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 $dT_{N}^{\text{inter}}/dp = 4.5$ 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 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 $T_c$ ($Pr$), 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 mechanical pressure and applied pressure demonstrates that while the Y substitution for Pr produces changes consistent

![Figure 5](image-url)
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 $dT_M^{\text{inter}}$ 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 $T_C \sim 334$ 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 $T_C$ (determined from the temperature of zero intercept in Figure 6(b)), demonstrates the ferromagnetic nature of the magnetic phase below $T_C$. The positive slopes of the Arrott plots around $T_C$ 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$_x$Mn$_2$Ge$_2$ and Pr$_{0.5}$Y$_{0.5}$Mn$_2$Ge$_2$ 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$_x$Mn$_2$Ge$_2$ and Pr$_{0.5}$Y$_{0.5}$Mn$_2$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 $T_C^{\text{inter}}$ for the Pr$_{1-x}$Y$_x$Mn$_2$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 Pr$_{1-x}$Y$_x$Mn$_2$Ge$_2$ compounds exhibit moderate isothermal magnetic entropy. As examples, the values of $-\Delta S_M$ for Ho$_2$Fe$_{17}$-Mn$_n$ 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 $\sim 330$ K. Dincer and Elerman [31] obtained maximum entropy values in the approximate range $-\Delta S_M \sim 2$–3 J kg$^{-1}$ K$^{-1}$ ($\Delta B=0$–5 T) around the paramagnetic to ferromagnetic Curie temperatures $T_C$ around 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. On the other hand a reduced entropy value of $-\Delta S_M \sim 1.8$ 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 $T_C \sim 340$ K [32].

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

$$|\Delta S_M^{PK}| \propto B^{2/3}$$  \hspace{1cm} (2)

where $-\Delta S_M^{PK}$ 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$_x$Mn$_2$Ge$_2$ compounds with $x=0.0$, 0.2 and 0.5 around $T_C^{\text{inter}}$. This agreement of $-\Delta S_M^{PK}$ 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$_x$Mn$_2$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$_2$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$_x$Mn$_2$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 Pr$_{1-x}$Y$_x$Mn$_2$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 Pr$_{1-x}$Y$_x$Mn$_2$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$_2$Ge$_2$ and (b) Pr$_{0.8}$Y$_{0.2}$Mn$_2$Ge$_2$. (c) Dependence of $-\Delta S_{M_{peak}}$ (peak value of the magnetic entropy change at different B) on the parameter $B^{2/3}$ for Pr$_{1-x}$Y$_x$Mn$_2$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.

Acknowledgements

This work is supported in part by Discovery Grant DP110102386 from the Australian Research Council. The work is also supported in part by a grant from the Australian Institute of Nuclear Science and Engineering and the Access to Major Research Facilities Program. The contributions from S. X. Dou, R. Zeng and Z. X. Cheng (University of Wollongong), A.J. Studer (ANSTO) and L. Caron, E. Brück (TU Delft) with whom we have collaborated on aspects of this overall project, are acknowledged.

References