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Magnetic properties of $Pr_{1-x}Y_xMn_2Ge_2$ compounds

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Abstract. The structure and magnetic properties of the $Pr_{1-x}Y_xMn_2Ge_2$ compounds (x = 0–1.0) have been investigated. All the compounds crystallize in $ThCr_2Si_2$-type structure. Substitution of Y for Pr led to a monotonic decrease in the lattice constants and the unit-cell volume. Samples in this alloy system exhibit a crossover from ferromagnetic ordering for $PrMn_2Ge_2$ to antiferromagnetic ordering for YMn_2Ge_2 as a function of concentration. The low-temperature behaviours of samples in the range $0 \leqslant x \leqslant 1.0$ were studied using magnetic measurements. Based on the magnetic measurements the tentative magnetic phase diagram showing three concentration regions of qualitatively different magnetic behaviour has been determined. Increasing substitution of Y for Pr in $PrMn_2Ge_2$ shows a depression of ferromagnetic ordering and the gradual development of antiferromagnetic ordering. For compounds with $0.4 \leqslant x < 0.7$ the magnetization first shows a clear ferromagnetic transition at $T_C \approx 330$ K, followed by a gradual drop at lower temperature, and then increases again. For compounds with $x < 0.4$ or $x \geqslant 0.7$, only ferromagnetic ordering or antiferromagnetic ordering occurs respectively.

1. Introduction

The ternary RMn_2X_2 compounds (R is rare earth, X is Ge or Si) crystallize in the body-centred tetragonal $ThCr_2Si_2$-type structure with space group $I4/mmm$, in which R, Mn and X atoms occupy the 2a, 4d and 4e sites, respectively [1, 2]. This structure can be described as a stacking of atomic layers in the sequence –Mn–X–R–X–Mn– along the c-axis. Over the last few years the magnetic properties of these compounds have been investigated by several research groups [3–7]. It is well known that the RMn_2X_2 compounds are either ferromagnetic or antiferromagnetic depending on the temperature, because the magnetic properties of RMn_2X_2 are very sensitive to the Mn–Mn distance, particularly to the intralayer Mn–Mn distance R^a_{Mn-Mn}. There is a critical value of R^a_{Mn-Mn} of about 2.85 Å: the coupling between the interlayer Mn moments is antiferromagnetic for $R^a_{Mn-Mn} < 2.85$ Å and ferromagnetic for $R^a_{Mn-Mn} > 2.85$ Å [3, 4]. With changing temperature the RMn_2X_2 compounds exhibit very interesting magnetic behaviour [2, 5]. It has been found that $PrMn_2Ge_2$ is a ferromagnet at high temperature with Curie temperature 334 K, and YMn_2Ge_2 is an antiferromagnet with Néel temperature 395 K [7]. This paper deals with the crystal structure and magnetic properties of the $Pr_{1-x}Y_xMn_2Ge_2$ compounds.

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2. Experimental details

The purity of the starting elements was as follows: Pr and Y, 99.9%; Mn, 99.99%; Ge, 99.999%. The $Pr_{1-x}Y_xMn_2Ge_2$ compounds with $x = 0$, 0.2, 0.4, 0.5, 0.6, 0.7, 0.8 and 1.0 were prepared by arc melting under argon atmosphere. Excess Mn was used to allow for loss during melting, and the ingots were remelted several times to ensure homogeneity. Samples were then annealed at 1073 K for two weeks in an evacuated quartz tube.

The single-phase nature of these compounds was established by x-ray analysis. X-ray diffraction of the powders was carried out using Cu Kα radiation and was adopted to check the crystal structure and determine lattice parameters.

The magnetizations of the samples were measured as a function of temperature and magnetic field using an extracting sample magnetometer (ESM) in the temperature range 5–300 K and a vibrating sample magnetometer (VSM) above 300 K. The magnetic field was 0.04 T to observe the magnetic transition, 0.7 T to determine the Néel temperature and up to 6.5 T to measure the magnetization processes. The magnetic transition temperatures T_C were derived from the thermal magnetic curves by extrapolating M^2–T plots to $M^2 = 0$. The transition temperatures T_1 and T_2 for compounds with $0.4 \leqslant x < 0.7$ were defined as the temperatures at which the temperature dependences of magnetization have the largest slopes. The saturation magnetization was derived by extrapolating M–$1/B$ plots to $1/B = 0$ using the higher-field parts of the magnetization curves.

3. Results and discussion

It has been found from x-ray diffraction patterns at room temperature that all compounds investigated are single phase and crystallize in $ThCr_2Si_2$-type structure. The x-ray diffraction patterns of $Pr_{1-x}Y_xMn_2Ge_2$ compounds with $x = 0.2$, 0.5 and 0.8 are shown in figure 1. The values of the lattice constants a and c, derived from x-ray diffraction patterns, and the unit-cell volume V are listed in table 1. It can be seen that substitution of Y for Pr results in a monotonic decrease in the lattice constants a and c and the unit-cell volume V with increasing Y content x. This may be associated with the smaller atomic radius of Y compared with that of Pr. As a consequence, the decrease of the lattice parameters results in the decrease of the intralayer nearest Mn–Mn distance R^a_{Mn-Mn} and interlayer nearest Mn–Mn distance R^c_{Mn-Mn}. The values of intralayer nearest Mn–Mn distance R^a_{Mn-Mn} are also listed in table 1. It can be seen that R^a_{Mn-Mn} also decreases monotonically with increasing Y content.

Results of magnetization measurements as a function of temperature show qualitatively different behaviours over different concentration ranges. Samples with $x < 0.4$ show only ferromagnetic (F) behaviour below $T_C \approx 330$ K (figure 2). The origin of the fact that as the temperature increases an increase in magnetization occurs at very low temperature is still not clear. One possible explain is that this may be associated with the domain wall pinning occurring at low temperature.

Samples in the range $0.4 \leqslant x < 0.7$ show three transitions as a function of temperature (figure 2). As temperature decreases magnetization shows a sharp increase at T_C followed by an approach to saturation state of ferromagnetic ordering. At $T_1 < T_C$ the alloy enters an intermediate (IM) phase in which an antiferromagnetic component in the internal magnetization develops as found in the $CeMn_2(Ge_xSi_{1-x})_2$ system [8], and finally at $T_2 < T_1$ the system goes from the IM phase to a ferromagnetic phase. M–B curves for $x = 0.5$ and 0.6 (figure 3) show linear antiferromagnetic behaviour at 100 K and saturation behaviour at 1.5, 25 and 280 K. Owing to inhomogeneity of the polycrystal samples, it is difficult

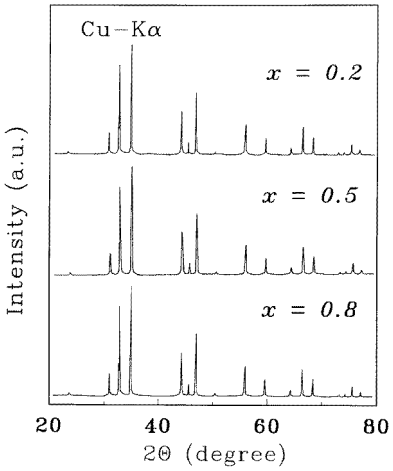


Figure 1. X-ray diffraction patterns at room temperature for the $Pr_{1-x}Y_xMn_2Ge_2$ compounds with $x = 0.2$, 0.5 and 0.8.

Table 1. The lattice constants a and c, the unit-cell volume V and the intralayer nearest Mn–Mn distance R^a_{Mn-Mn}, the magnetic transition temperature T_C, T_N, T_1 and T_2 and the saturation magnetization σ_S at 1.5 K for the $Pr_{1-x}Y_xMn_2Ge_2$ compounds.

x	a (Å)	c (Å)	V (Å^3)	R^a_{Mn-Mn} (Å)	T_C (K)	T_N (K)	T_1 (K)	T_2 (K)	σ_S (μ_B fu^{-1})
0	4.124	10.918	185.65	2.916	333				5.28
0.2	4.112	10.917	184.61	2.908	330				5.05
0.4	4.094	10.906	182.77	2.895	327		200	70	4.84
0.5	4.083	10.897	181.63	2.887	325		230	50	4.37
0.6	4.069	10.890	180.31	2.877	323		260	40	3.72
0.7	4.048	10.884	178.37	2.863		361			1.30
0.8	4.028	10.877	176.44	2.848		400			0.92
1.0	3.996	10.873	173.61	2.826		437			0.11

to determine the values of T_1 and T_2 accurately. Here the values of T_1 and T_2 are taken from those points at which the temperature dependence of magnetization has the maximum slope.

As shown in figure 4 samples with $x \geqslant 0.7$ show peaks in the temperature dependence of magnetization, coinciding with T_N, which move from 361 K for $x = 0.7$ to 437 K for $x = 1.0$. The M–B curves in this concentration range indicate an antiferromagnetic (AF) ordering (figure 5).

The results of magnetization measurements at 0.04 T are summarized in the phase diagram presented in figure 6. Three regions of qualitatively different magnetic behaviour can be determined. In region I ($0 \leqslant x < 0.4$) only ferromagnetic ordering is observed, although this range of samples was not investigated in detail. However, as shown in figure 7 saturation magnetization at 1.5 K was found to decrease slowly with increasing Y concentration. Since the magnetic ordering in this series is due to the interaction of Mn moments, this decrease in saturation magnetization either may be a result of incomplete mixing of Y with Pr in the lattice resulting in clusters of ferromagnetic $PrMn_2Ge_2$, or may

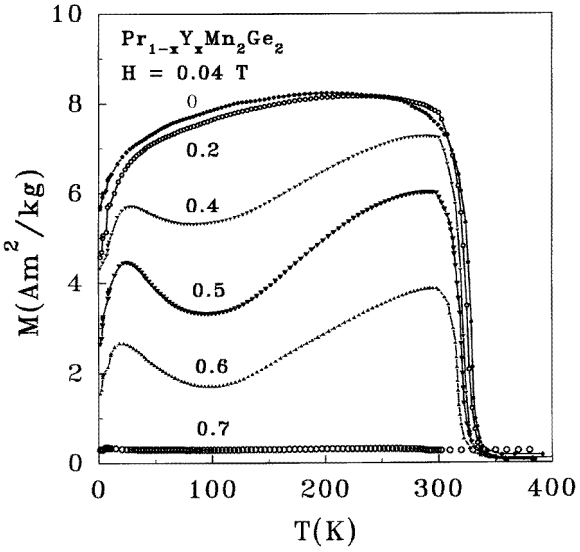
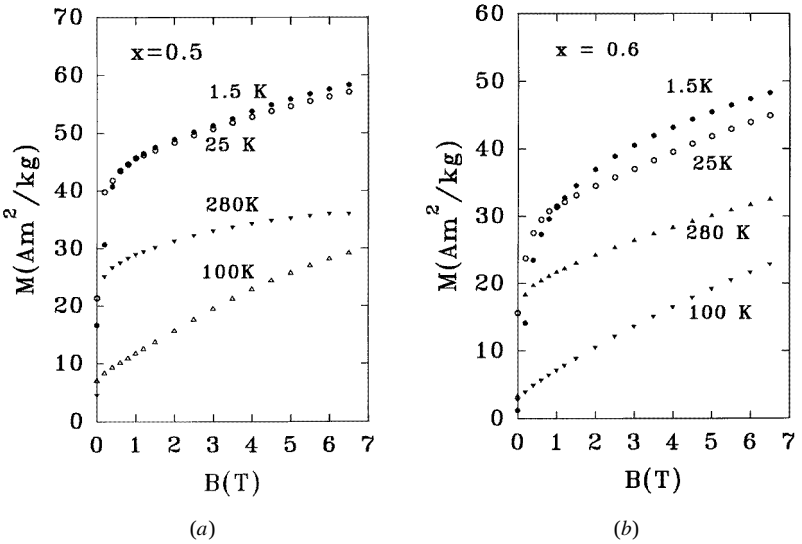


Figure 2. The temperature dependence of the magnetization M in a field of 0.04 T in the temperature range 5–380 K for the $Pr_{1-x}Y_xMn_2Ge_2$ compounds.



(*a*) (*b*)

Figure 3. The magnetization curves at 1.5, 25, 100 and 280 K for $Pr_{1-x}Y_xMn_2Ge_2$ compounds: (*a*) $x = 0.5$, (*b*) $x = 0.6$.

be a result of extreme sensitivity of an individual Mn atom to its near-neighbour interactions which, at some critical content of Y neighbours, will order ferromagnetically with respect to adjacent Mn planes. This picture is consistent with 'site models' [9] of magnetic interactions, in which the magnetic ordering of a moment depends on the short-range nearest-neighbour interactions. Apart from this, another possibility for the change in this region is the formation of ferromagnetic clusters of composition $Pr_{1-x}Y_xMn_2Ge_2$ which respond to some average

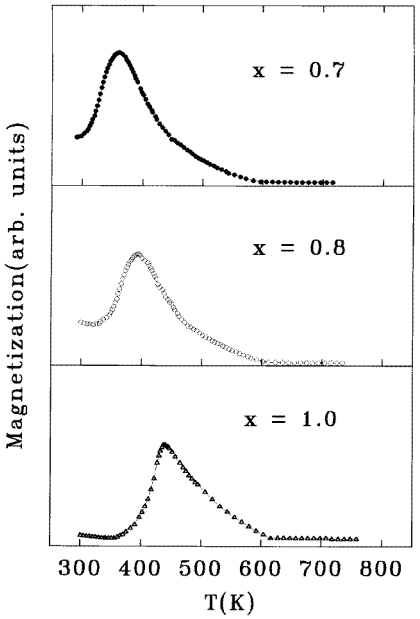


Figure 4. The temperature dependence of the magnetization M in a field of 0.7 T in the temperature range 300–750 K for the $Pr_{1-x}Y_xMn_2Ge_2$ compounds.

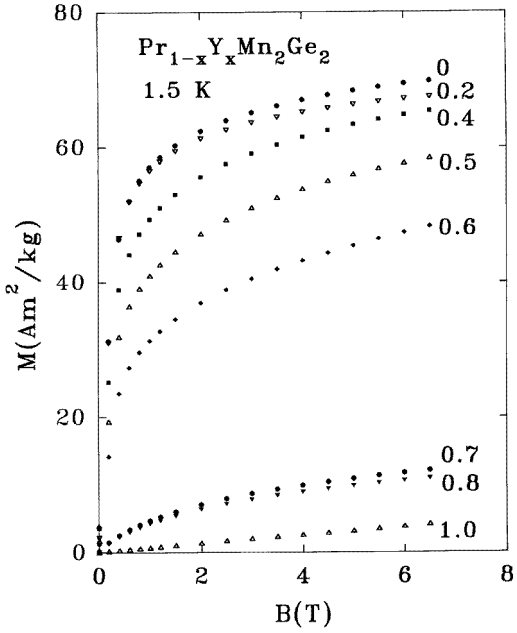


Figure 5. The magnetization curves at 1.5 K for $Pr_{1-x}Y_xMn_2Ge_2$ compounds.

field produced by the moments (cluster model [9, 10]). These magnetically ordered clusters decrease in number and size with increasing Y concentration. Either the cluster model or

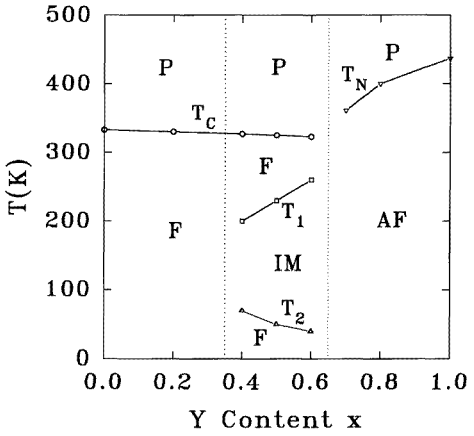


Figure 6. The magnetic phase diagram of the $Pr_{1-x}Y_xMn_2Ge_2$ system.

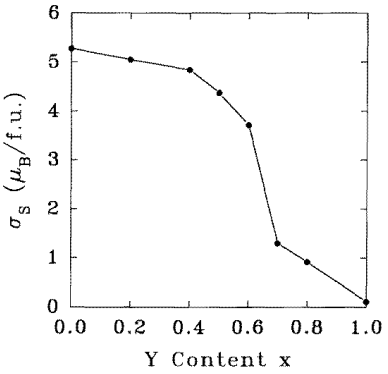


Figure 7. The saturation magnetization as a function of Y concentration for $Pr_{1-x}Y_xMn_2Ge_2$ compounds.

the site model might explain the change of saturation magnetization observed in this region.

In region II ($0.4 \leqslant x < 0.7$) an indentation in magnetization is observed. The magnitude of the magnetization at 1.5 K (figure 7) is seen to decrease rapidly with increasing Y content in this region. Along with the M–B measurements, indicating both ferromagnetic and antiferromagnetic interactions, this is consistent with the idea of the growth of antiferromagnetic clusters in the ferromagnetic host. However, it is also consistent with the site model. At some concentration it becomes statistically probable that most Mn atoms are bordered by the critical number of Y atoms producing locally antiferromagnetically aligned Mn moments. As shown in the magnetization in figure 2, the higher the Y content, the more antiferromagnetic order is preferred. So the magnetization of $Pr_{0.4}Y_{0.6}Mn_2Ge_2$ (figure 8) is somewhat like that of $SmMn_2Ge_2$ compound [3]. The fact that the linewidth of x-ray diffraction peaks for the compound with $x = 0.5$ is a little larger than that for compounds with $x = 0.2$ and 0.8 (figure 1) confirms the existence of fluctuations in Pr/Y site occupancy or magnetic clusters.

Samples in region III ($0.7 \leqslant x \leqslant 1.0$) show only a transition from antiferromagnetic state to paramagnetic (P) state as temperature increases. This may be caused by the fact

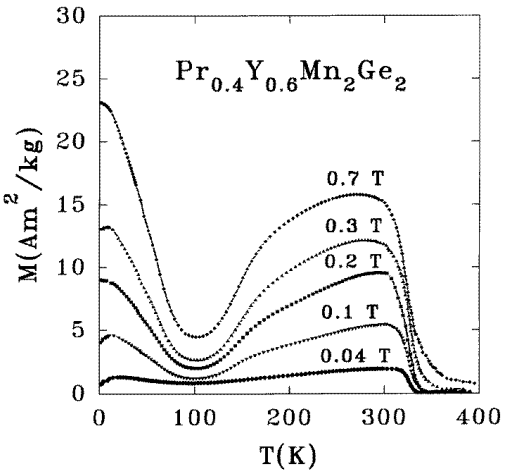


Figure 8. The thermal magnetic curves at different fields for $Pr_{0.4}Y_{0.6}Mn_2Ge_2$ compounds.

that the intralayer nearest Mn–Mn distance R^a_{Mn-Mn} is near to or smaller than the critical value of about 2.85 Å (see table 1).

4. Conclusion

In conclusion, all the $Pr_{1-x}Y_xMn_2Ge_2$ compounds with $x = 0$–1.0 crystallize in $ThCr_2Si_2$-type structure. Substitution of Y for Pr led to a monotonic decrease in the lattice constants a and c and the unit-cell volume V from $a = 4.124$ Å, $c = 10.918$ Å and $V = 185.65$ Å^3 for $x = 0$ to $a = 3.996$ Å, $c = 10.873$ Å and $V = 173.61$ Å^3 for $x = 1.0$. The intralayer nearest Mn–Mn distance R^a_{Mn-Mn} decreases monotonically from 2.916 Å for $x = 0$ to 2.826 Å for $x = 1.0$. Samples in this alloy system exhibit a crossover from ferromagnetic ordering for $PrMn_2Ge_2$ to antiferromagnetic ordering for YMn_2Ge_2 as a function of Y concentration. From the magnetization measurements the magnetic phase diagram, which shows three concentration regions of qualitatively different magnetic behaviour, has been determined. Increasing substitution of Y for Pr in $PrMn_2Ge_2$ shows a depression of ferromagnetic ordering and the gradual development of antiferromagnetic ordering. For compounds with $0.4 \leqslant x < 0.7$, with decreasing temperature, the magnetization first shows a clear ferromagnetic transition at $T_C \approx 330$ K, followed by a gradual drop at lower temperatures, and then increases again. For compounds with $x < 0.4$ or $x \geqslant 0.7$, only ferromagnetic ordering or antiferromagnetic ordering occurs respectively.

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