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2004 J. Phys.: Condens. Matter 16 4955

(http://iopscience.iop.org/0953-8984/16/28/015)

INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **16** (2004) 4955–4962 PII: S0953-8984(04)77518-9

Magnetic characterization of intermetallic $PrMn_2Ge_{2-x}Si_x$ compounds by AC susceptibility, x-ray diffraction and differential scanning calorimetry studies

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Received 10 March 2004
Published 2 July 2004
Online at stacks.iop.org/JPhysCM/16/4955
doi:10.1088/0953-8984/16/28/015

Abstract

X-ray powder diffraction, AC susceptibility and differential scanning calorimetry (DSC) studies were performed on the polycrystalline $PrMn_2Ge_{2-x}Si_x$ ($0 \leqslant x \leqslant 2$) compounds. All compounds investigated crystallize in the body-centred tetragonal $ThCr_2Si_2$-type structure with the space group $I4/mmm$. Substitution of Si for Ge leads to a linear decrease of the lattice constants and the unit cell volume. The lattice constants and the unit cell volume obey Vegard's law. Samples in this alloy system exhibit a crossover from ferromagnetic ordering for $PrMn_2Ge_2$ to antiferromagnetic ordering for $PrMn_2Si_2$ as a function of Si concentration x. At low temperatures, the Pr sublattice also orders for $x \leqslant 0.4$. The samples with $x \leqslant 1.3$ are ferromagnetic and have spin reorientation temperatures just below the Curie temperature. In the cases of $x = 1.2$ and 1.3, re-entrant ferromagnetism is observed. The samples with $x \geqslant 1.6$ are antiferromagnetic below the Néel temperature T_N(Mn). By comparing our results to earlier neutron diffraction and Mössbauer studies, the x–T magnetic phase diagram has been constructed.

1. Introduction

Recently, the ternary intermetallic compounds RT_2X_2 (R is rare earth, T is transition metal and X is Si or Ge) have been extensively studied due to their many interesting physical properties ranging from superconductivity to heavy fermion behaviour [1, 2]. These compounds crystallize in the well known body-centred tetragonal $ThCr_2Si_2$-type structure with the space group $I4/mmm$, in which R, T and X atoms occupy 2a (0, 0, 0), 4d (0, 1/2, 1/4) and 4e

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$(0, 0, z)$ sites, respectively [3]. The structure is made up of atomic layers stacked along the c-axis direction with the sequence T–X–R–X–T. This layered crystal structure leads to a variety of magnetic properties and complex magnetic behaviour [4–8]. It has been reported that the most of the compounds carry no magnetic moment on the transition metal (T), while the Mn sublattice orders magnetically in the RMn_2X_2 compounds [9]. Among studies of these compounds, many have been devoted to unusual magnetic properties of $SmMn_2Ge_2$ [10–14]. These studies revealed re-entrant ferromagnetism and five magnetic phase transitions in $SmMn_2Ge_2$, $T_{Sm} \sim 30$ K, $T_{F,AF} \sim 100$ K, $T_{AF,F} \sim 150$ K, $T_{F,AF} \sim 345$ K and $T_N \sim 385$ K.

Earlier neutron scattering investigations on RMn_2X_2 compounds have shown that the Mn atoms carry a magnetic moment, and that long-range magnetic ordering of the Mn moments occurs. The nature of the magnetic coupling within and between the Mn layers in these compounds is closely related to the in-plane Mn–Mn spacing d^a_{Mn-Mn}. Roughly, if $d^a_{Mn-Mn} > 2.87$ Å ($a > 4.06$ Å), the intralayer in-plane coupling is antiferromagnetic and the interlayer coupling is ferromagnetic. In the case 2.84 Å $< d^a_{Mn-Mn} < 2.87$ Å (4.02 Å $< a < 4.06$ Å), both the intralayer in-plane coupling and the interlayer coupling are antiferromagnetic. When $d^a_{Mn-Mn} < 2.84$ Å ($a < 4.02$ Å), there is no intralayer in-plane spin component, and the interlayer coupling remains antiferromagnetic. On the other hand, the Mn moments have components along both the c-axis and the (001) plane for the light rare-earth compounds. The interlayer Mn moment alignment along the c-axis becomes either ferromagnetic or antiferromagnetic depending on the value of d^a_{Mn-Mn}, while the intralayer in-plane components of the Mn moments are antiferromagnetically coupled. The in-plane antiferromagnetism can be commensurate or incommensurate with the lattice periodicity. When R is a heavy rare-earth element in RMn_2Ge_2, the moments in the Mn layers align parallel along the c-axis, and there is no in-plane component [15–19].

In $PrMn_2Ge_2$, intralayer in-plane antiferromagnetic ordering (AFl) occurs below the Néel temperature $T_N = 415$ K. Cooling to temperatures below the Curie temperature $T_C = 330$ K leads to a canted spin structure (Fmc) with the c-axis interlayer spin components aligning parallel. The canting angle from the c-axis is about 65°. Below 280 K, the magnetic structure transforms from a canted to a conical configuration (Fmi) with a cone semiangle of approximately 58°. The c-axis interlayer alignment remains parallel. The Pr sublattice moments are magnetically disordered at these high temperatures and order along the c-axis parallel to the Mn moments only below $T_C(Pr) = 80$ K. The magnetic structure of the Mn sublattice below this temperature remains conical. The intralayer in-plane coupling of the Mn moments is always antiferromagnetic from T_N down to the lowest temperatures. The in-plane antiferromagnetic structure is collinear for 280 K $< T < T_N$ and has an incommensurate configuration for $T < 280$ K [1, 9, 12, 15, 20, 21]. $PrMn_2Si_2$ is antiferromagnetic below $T_N(Mn) = 348$ K. The magnetic moment of the Pr sublattice in $PrMn_2Si_2$ is not ordered at low temperatures [9, 12, 15, 22].

In this paper we are interested in the effects of the Si substitution for Ge on the crystal structure and magnetic properties of $PrMn_2Ge_{2-x}Si_x$ compounds. It would be attractive to study the properties of $PrMn_2Ge_{2-x}Si_x$ system to gain a deeper insight into intralayer and interlayer magnetic interactions. Therefore, we present results on the study of the magnetic properties of $PrMn_2Ge_{2-x}Si_x$ investigated by low field AC susceptibility and DSC measurements as an extension of earlier studies on $RMn_2Ge_{2-x}Si_x$ [23–26].

2. Experimental details

$PrMn_2Ge_{2-x}Si_x$ compounds with $x = 0.0, 0.4, 0.8, 1.0, 1.2, 1.3, 1.6$ and 2.0 were prepared by arc melting under argon atmosphere of appropriate amounts of Pr(99.9%), Mn(99.98%),

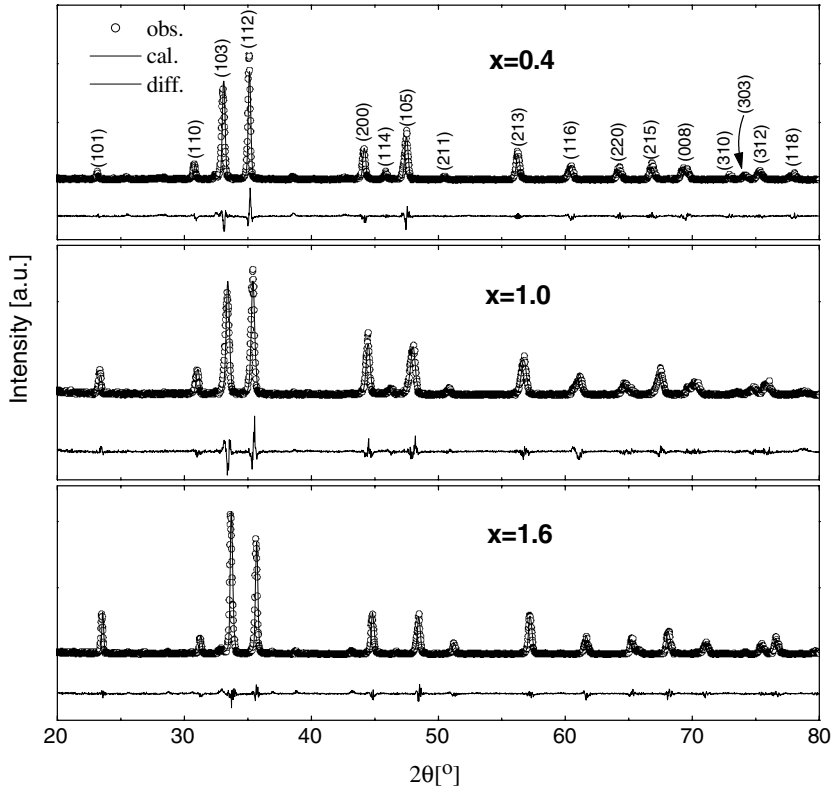

Figure 1. The profile fitting for some selected $PrMn_2Ge_{2-x}Si_x$ compounds.

Ge(99.9999%) and Si(99.95%) in a water-cooled copper boat. The mass loss of Mn during the melting was compensated by adding the 2% excess Mn over the stoichiometric amount. The polycrystalline ingots were turned over and remelted several times to ensure good homogeneity. X-ray diffraction studies were carried out by using a Brucker D8 Advance diffractometer equipped with Cu Kα radiation. The profile fitting was performed using the FULLPROF [27] program.

The characterization of the samples by differential scanning calorimetry (DSC) was performed using DSC 2010 (TA Instruments) in an alumina box under protective nitrogen gas above room temperature. The heating ramp was run at 20 K min^{-1}. The AC magnetic susceptibility as a function of temperature was measured by means of a Lake Shore 7130 AC magnetometer in the temperature range 15–325 K in a magnetic field of 80 A m^{-1} and 111 Hz frequency.

3. Results and discussion

X-ray diffraction patterns at room temperature indicated that all compounds are single phase and crystallize in the $ThCr_2Si_2$-type structure with the space group $I4/mmm$. Figure 1 presents the results of the profile fitting of the powder patterns for some selected samples. The refined unit cell parameters a and c, in-plane Mn–Mn spacing d^a_{Mn-Mn} and unit cell volume V are given in table 1, while figure 2 illustrates a, c, d^a_{Mn-Mn} and V as a function of x. The lattice parameters a and c and unit cell volume V obey Vegard's law. The decreases of these parameters may be associated with the smaller atomic radius of Si compared with Ge. The

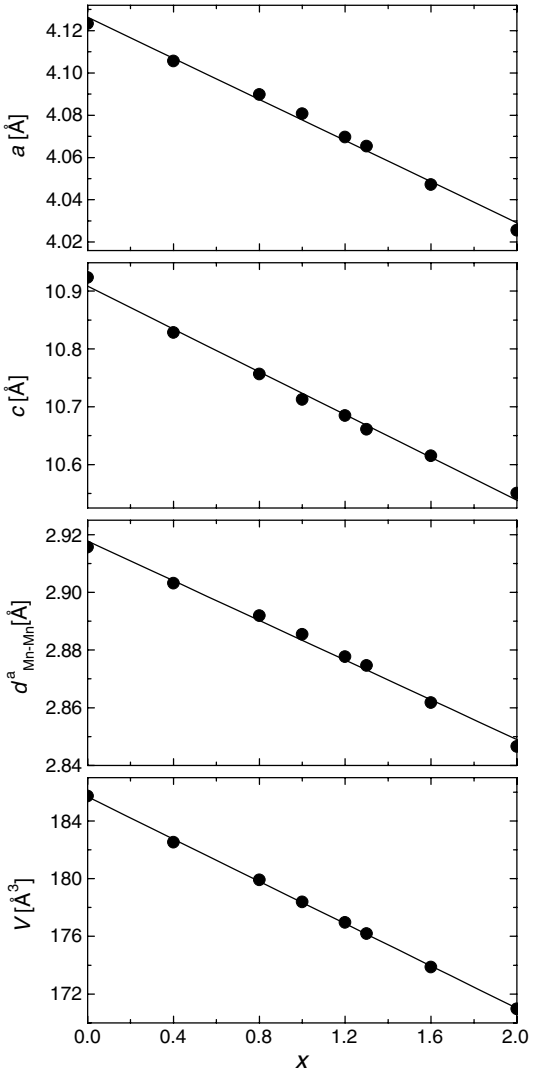

Figure 2. Variation of the lattice constants a and c, $d^a_{\mathrm{Mn-Mn}}$ and the unit cell volume V with Si concentration x at room temperature for the $PrMn_2Ge_{2-x}Si_x$ compounds.

lattice parameters for $x = 0$ and 1 are in good agreement with values reported previously in the literature [15, 20, 21]. For the samples with $x \leqslant 1.3$, the in-plane Mn–Mn spacing $d^a_{\mathrm{Mn-Mn}}$ exceeds the critical in-plane Mn–Mn distance (2.87 Å). The expected parallel alignment of the Mn interlayer moment at these concentrations is observed at T_{C}(Mn).

Figure 3 shows the heat flow of the sample during the heating from 123 to 573 K at a constant ramp of 20 K min^{-1}. In this temperature range, endothermic reactions corresponding to the magnetic phase transitions take place for the samples. The transition temperatures obtained by DSC measurements below room temperature, T_{C}(Mn) and T_2, are in good agreement with the AC susceptibility results as can be seen in table 2. Above room temperature, endothermic reactions indicating the Néel temperature occur at about 400 K. Up to now, the Néel temperature for $PrMn_2Ge_2$ could only be found by neutron scattering and Mössbauer studies. In the present work, we also observed this transition temperature T_{N}(Mn) from our DSC results which is in good agreement with previously reported findings [12, 17].

Table 1. The lattice constants a and c, the unit cell volume V and the in-plane Mn–Mn spacing $d^a_{\mathrm{Mn-Mn}}$ for the $PrMn_2Ge_{2-x}Si_x$ compounds.

x	a (Å)	c (Å)	V (Å^3)	$d^a_{\mathrm{Mn-Mn}}$ (Å)
0.0	4.1233	10.9236	185.7	2.9156
0.4	4.1056	10.8284	182.5	2.9031
0.8	4.0898	10.7565	179.9	2.8919
1.0	4.0807	10.7124	178.4	2.8855
1.2	4.0697	10.6847	177.0	2.8777
1.3	4.0653	10.6610	176.2	2.8746
1.6	4.0471	10.6154	173.9	2.8618
2.0	4.0256	10.5505	171.0	2.8465

Table 2. The magnetic phase transition temperatures obtained by AC susceptibility and DSC measurements.

	AC susceptibility results					DSC results			
x	T_{Pr} (K)	T_1 (K)	T_2 (K)	T_{SR} (Mn) (K)	T_{C} (Mn) (K)	T_2 (K)	T_{SR} (Mn) (K)	T_{C} (Mn) (K)	T_{N} (Mn) (K)
0.0	71			294			288	330	416
0.4	74			318				324	428
0.8				303	323			315	425
1.0		62	180	293	313			312	416
1.2		52	235	280	306	258	272	298	394
1.3		50	245	278	307	250	264	303	376
1.6				118					329
2.0				53					355

The temperature dependence of the AC magnetic susceptibility $\chi_{\mathrm{AC}}(T)$ of the $PrMn_2Ge_{2-x}Si_x$ series is displayed in figure 4 in an applied field of 80 A m^{-1} and 111 Hz frequency. Results of the AC susceptibility measurements as a function of temperature show qualitatively different behaviours over different concentration ranges. The ferromagnetic ordering is seen just above room temperature for $x \leqslant 1.3$. The data for $x = 0$ show a distinct feature at 294 K. This transition temperature T_{SR}(Mn) corresponds to the temperature of the transition from the canted (Fmc) to the conical (Fmi) spin structure. Note that the appearance of the AC susceptibility curve for $x \leqslant 1.3$ is similar in the sense that it exhibits similar features at about 290 K. These temperatures agree more or less with those of earlier neutron investigations and it is therefore concluded that the magnetic ordering is the same as stated in these investigations [15]. The ordering of the Pr sublattice for $x = 0$ is observed as a small increase at $T_{\mathrm{C}}(\mathrm{Pr}) = 71$ K. For the sample with $x = 0.4$, the change of slope at 74 K can be attributed to T_{C}(Pr). The susceptibility decreases with decreasing temperature at very low temperatures for the samples with $x \leqslant 1.3$. Similar behaviour was also observed for $Pr_{1-x}Y_xMn_2Ge_2$ compounds [21]. This effect can be attributed to the possibility that the antiferromagnetic interactions become dominant and ferromagnetic components are pinned at below and around 150 K. It was reported that the pinning of the ferromagnetic components were caused by the high anisotropy of the antiferromagnetic component as in [28]. At $T_2 < T_{\mathrm{C}}(\mathrm{Mn})$, the sample with $x = 1.0$ enters an intermediate phase (IM) in which an antiferromagnetic component in the interval magnetization develops as found in $Pr_{1-x}Y_xMn_2Ge_2$ [21] and $CeMn_2(Ge_xSi_{1-x})_2$ [29]. We have determined T_1 and T_2 from the derivation of the susceptibility data with respect to temperature. We simply

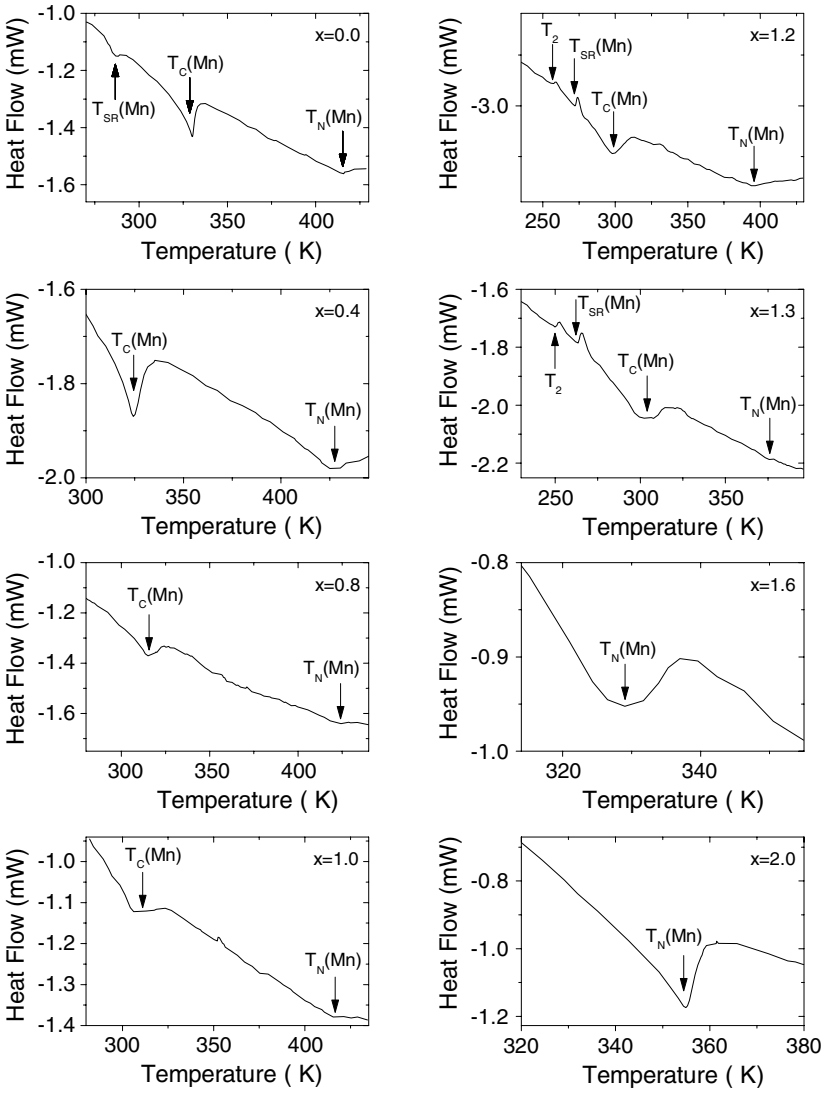

Figure 3. DSC measurements for the $PrMn_2Ge_{2-x}Si_x$ compounds.

denoted the minimum as T_1 and the maximum as T_2. T_2 can also be determined from DSC measurements. The $SmMn_2Ge_2$-like magnetic behaviour has been observed for the samples with $x = 1.2$ and 1.3. Upon cooling, these samples reach a ferromagnetic (Fmc) phase at T_C(Mn), a ferromagnetic (Fmi) phase at T_{SR}(Mn), an antiferromagnetic phase at T_2 and again a ferromagnetic phase at T_1. Similar re-entrant ferromagnetism was previously observed in $NdMn_{2-x}Fe_xGe_2$ [30], $Nd_{1-x}La_xMn_2Si_2$ [31] and $PrMn_{2-x}Fe_2Ge_2$ [32]. For the samples with $x = 1.2$ and 1.3, at room temperature, the lattice constant a is very close to the critical in-plane Mn–Mn distance. For the samples with $x = 1.6$ and 2.0, a small peak is seen, at 118 and 53 K, respectively. These temperatures may correspond to the spin reorientation transition for the Mn sublattice as observed in $PrMnSi_2$ [33].

The magnetic phase diagram for $PrMn_2Ge_{2-x}Si_x$, summarizing the AC susceptibility and DSC measurements, is presented as figure 5. The transition temperatures are also listed in table 2. By making use of the known magnetic structures of $x = 0$ and 2 from DC magnetization,

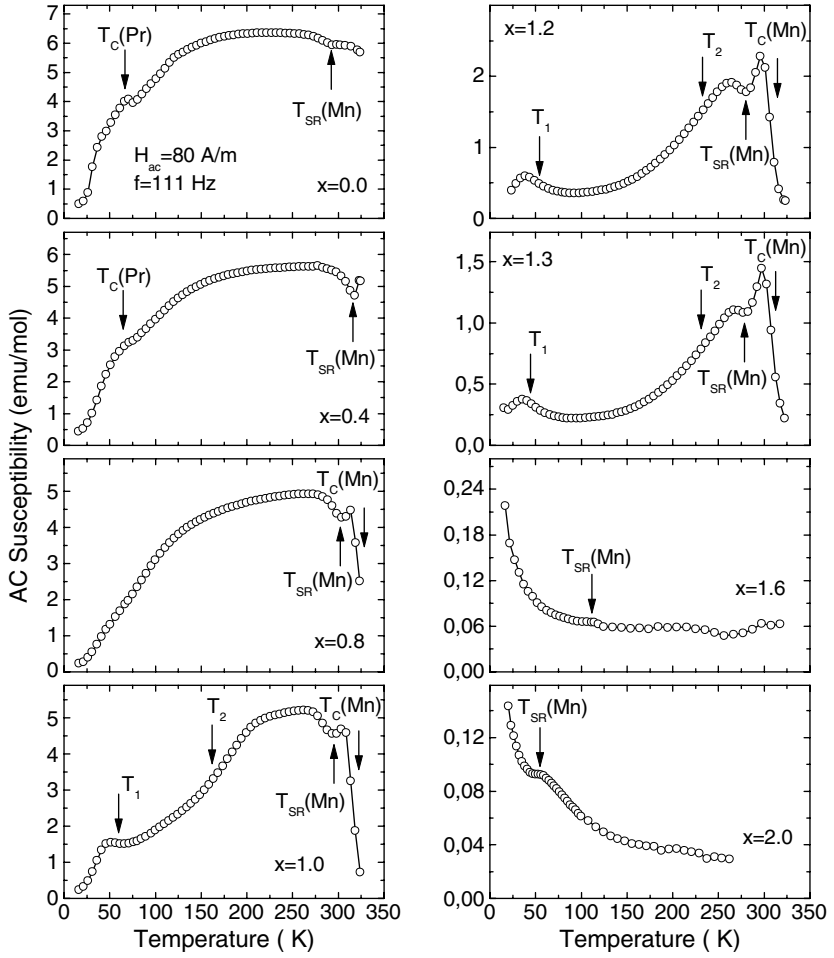

Figure 4. AC magnetic susceptibility as a function of temperature for $PrMn_2Ge_{2-x}Si_x$ compounds.

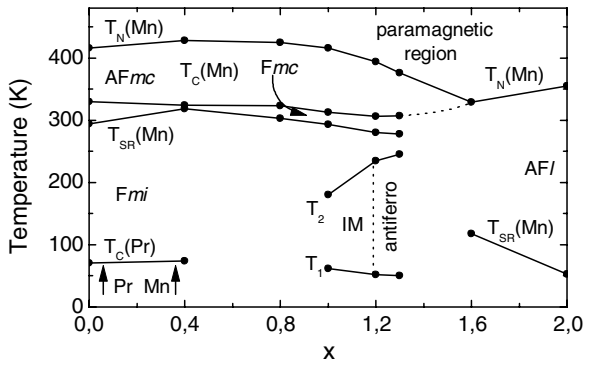

Figure 5. The magnetic phase diagram of $PrMn_2Ge_{2-x}Si_x$ compounds.

neutron diffraction and Mössbauer studies [1, 9, 12, 15, 20–22], the low field AC magnetic susceptibility may give information on the magnetic structure of the compounds at intermediate concentrations. Therefore, we may tentatively construct a magnetic phase diagram. This diagram is mainly characterized by the occurrence of five magnetic phases denoted with the notation given in [30]. T_N(Mn) was connected to T_C(Mn) to define the AF*mc* phase region.

4. Conclusions

All the $PrMn_2Ge_{2-x}Si_x$ compounds crystallize in the $ThCr_2Si_2$-type structure. Substitution of Si for Ge causes a linear decrease in the lattice constants and unit cell volume from $a = 4.1233$ Å, $c = 10.9236$ Å and $V = 185.7$ Å^3 for $x = 0$ to $a = 4.0256$ Å, $c = 10.5505$ Å and $V = 171.0$ Å^3 for $x = 2$. Ferromagnetism observed in $PrMn_2Ge_2$ transforms to antiferromagnetism with the substitution of Si for Ge. Re-entrant ferromagnetism is observed for the samples with $x = 1.2$ and 1.3. The x–T magnetic phase diagram has been proposed from the derived transition temperatures of the present investigations in combination with the earlier reported magnetic structures.

Acknowledgments

The authors would like to thank to Dr Erhan AKSU for helping during the DSC measurements. This work was supported by State Planning Organization of Turkey (DPT) under grant number 2002-K-120130-5.

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