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Magnetic ordering of the Pr sublattice with the substitution of Cu for Mn in $PrMn_2Si_2$ intermetallics

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Abstract

The magnetic properties of $PrMn_{2-x}Cu_xSi_2$ ($0 \leqslant x \leqslant 1$) were studied by field-cooled and zero-field-cooled magnetization measurements in the temperature range 5 K $\leqslant T \leqslant$ 350 K in low external fields (5 mT) and by magnetic-field-dependent magnetization measurements in fields up to 5.5 T. Substitution of Cu for Mn leads to a linear decrease in the lattice constant c and the unit cell volume V and a linear increase in the lattice constant a. Earlier neutron diffraction experiments showed that Pr does not order down to 1.6 K in $PrMn_2Si_2$ while the ferromagnetic Mn planes are ordered antiparallel along the c axis. With the increasing Cu content, the magnetization increases rapidly at low temperatures for the samples with $0.4 \leqslant x \leqslant 1$. Cu substitution strongly changes the magnetic properties and leads to the magnetic ordering of the Pr sublattice. This is mainly deduced from the discussion of the values of the magnetic moments at low temperatures. Below the Curie temperatures T_C, the spins in the Mn sublattice are arranged parallel to the Pr sublattice. With increasing Cu, $T_C(x)$ has a maximum value of 155 K at $x = 0.6$ and decreases for samples with $x \geqslant 0.7$.

1. Introduction

In the last two decades, the ternary intermetallic compounds RMn_2X_2 (R = rare-earth, X = Si or Ge) have been extensively studied due to the their unusual magnetic properties and other physical properties including superconductivity, mixed valence, heavy fermion and Kondo behaviour [1, 2]. Most of these compounds crystallize in the body-centred tetragonal $ThCr_2Si_2$-type structure with space group $I4/mmm$, in which the R, Mn and X atoms occupy the

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2a (0, 0, 0), 4d (0, 1/2, 1/4) and 4e (0, 0, z) positions, respectively [3]. A stacking of the atomic layers along the c axis direction with the sequence R–X–Mn–X–R forms this structure. From the magnetic point of view, RMn_2X_2 compounds have two different magnetic subsystems, R and Mn subsystems, and their magnetic properties are mainly determined by these two subsystems and their interactions [1, 2].

Neutron diffraction and magnetic studies of RMn_2Ge_2 compounds with light rare earths have shown that with decreasing temperature the manganese subsystem undergoes a transition from an antiferromagnetic state to a ferromagnetic state [4, 5]. The Néel temperature of these compounds lies in the range 390–410 K, and the Curie temperature is about 330 K. The magnetic ordering of the rare-earth subsystem in RMn_2Ge_2 compounds with the light rare earths Pr and Nd is about 100 K. In RMn_2Si_2, however, neutron diffraction experiments [6] showed that the Pr magnetic moments do not order above 1.6 K, while a ferromagnetic ordering of the Nd sublattice occurs below 33 K. In $PrMn_2Si_2$, the ferromagnetic Mn planes are aligned antiparallel along the c axis below 368 K. Since the magnetic coupling within and between the Mn layers has a strong dependence on the *intra*layer Mn–Mn exchange interaction [1], one can vary this coupling by the replacement of Mn by another transition metal atom and this leads to different changes of the magnetic properties. In the present paper, we report on the magnetic properties of $PrMn_{2-x}Cu_xSi_2$, studied by magnetic measurements to elucidate the influence of the substitution of Cu for Mn on the magnetic behaviour of $PrMn_2Si_2$.

2. Experimental details

The $PrMn_{2-x}Cu_xSi_2$ samples with $x = 0$, 0.2, 0.4, 0.5, 0.6, 0.7, 0.8 and 1 were prepared by induction melting under Ar atmosphere in a water-cooled copper boat. The purities of the elements were 99.9% for Pr, 99.98% for Mn and Cu and 99.9999% for Si, respectively. Adding 2% excess Mn over the stoichiometric amount compensated the mass loss of Mn during melting. The polycrystalline ingots were turned over and remelted several times to ensure homogeneity, followed by annealing at 1073 K for 10 days in evacuated quartz tubes. The samples were characterized by x-ray powder diffraction on a Siemens D-500 diffractometer using Cu Kα radiation and a secondary monochromator.

The temperature and magnetic field dependences of the magnetization for 5 K $\leqslant$ $T \leqslant$ 350 K were measured using a superconducting quantum interference device (SQUID) magnetometer from Quantum Design. In the SQUID magnetometer, the temperature-dependent magnetization measurements were carried out in an external field of 5 mT. The samples were first heated to 350 K and subsequently cooled to 5 K in zero external magnetic field. The measurements were performed in a zero-field-cooled (ZFC) and field-cooled (FC) sequence. The field dependence of the magnetization was measured up to 5.5 T.

3. Results and discussion

X-ray diffraction patterns at room temperature indicated that all compounds are single phases and crystallize in the $ThCr_2Si_2$-type structure with the space group $I4/mmm$. Figure 1 illustrates V, a, c and c/a as a function of x. Substitution of Cu for Mn leads to a linear decrease in the lattice constant c and the unit cell volume V and a linear increase in the lattice constant a and is seen in all the samples investigated in this work.

The temperature dependences of zero-field-cooled (ZFC) and field-cooled (FC) magnetizations of $PrMn_{2-x}Cu_xSi_2$ in an external field of 5 mT are shown in figure 2. Earlier neutron diffraction experiments indicated that the ferromagnetic (001) Mn planes in $PrMn_2Si_2$ are aligned antiparallel along the c axis below 368 K [6]. Mainly, the $x = 0$ sample

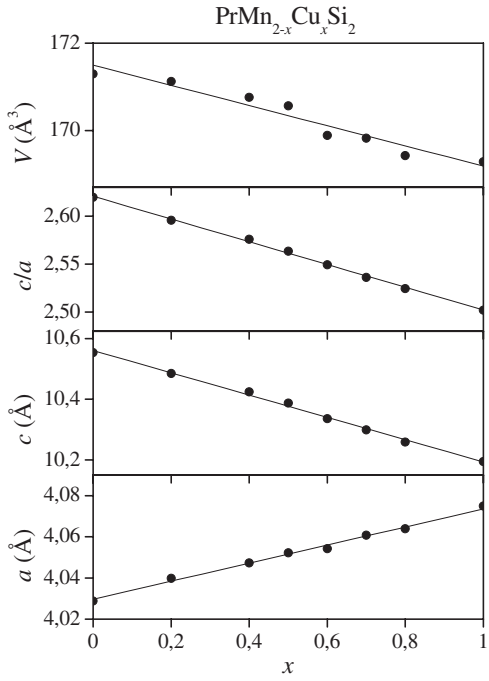

Figure 1. The variation of the lattice constants c and a, c/a and unit cell volume V with Cu content at room temperature for $PrMn_{2-x}Cu_xSi_2$.

is antiferromagnetic. But, the Néel temperature for this compound is not observed up to 350 K and also not observed for the other compounds. Magnetization of this sample is almost constant between 240 and 350 K, but below 240 K magnetization shows a gradual increase with decreasing temperature. At very low temperature, magnetization increases rapidly. This increase, along with the splitting between the ZFC and FC curves, may suggest that a weak ferromagnetic component in a direction other than along the c axis develops due to some non-collinearity in the antiferromagnetic alignment. This behaviour was not observed in the previous high field magnetization measurements and in the neutron diffraction experiments [6, 7]. This increase in $M(T)$ and splitting between ZFC and FC curves continues for the $x = 0.2$ sample.

With further substitution of Cu for Mn, magnetization of the samples with $0.4 \leqslant x \leqslant 1$ begins to increase rapidly at low temperatures. This increase is related to the ferromagnetic ordering, and the corresponding Curie temperatures are shown in figure 2. T_C is estimated from the inflection point of the magnetization curves. Below the Curie temperatures, the magnetic field dependences of the magnetization for these samples at different temperatures (figure 3) also indicate the ferromagnetic behaviour. It is expected that this ferromagnetic ordering is related to the ferromagnetic ordering of Mn planes along the c axis, since neutron diffraction experiments [6] showed that the Pr magnetic moments do not order above 1.6 K. Figure 4 shows the hysteresis loops for the $x = 0.5$ sample at 5, 50, 110 and 180 K. Saturation is not attained at any temperature up to 5.5 T. For the $x = 0.5$ sample at 5 K, the value of maximum magnetization is about 2.13 μ_B per Mn atom at 5.5 T, higher than the value of 1.94 μ_B for the $x = 0$ sample as found in the neutron diffraction studies on $PrMn_2Si_2$ [6]. However, it is expected that the value of Mn magnetization decreases gradually with the substitution of Cu for Mn as in $LaMn_{2-x}Cu_xGe_2$ from 1.5 μ_B per Mn atom for $x = 0$ to 1.0 μ_B per Mn atom for $x = 1$ [8]. In contrast, there is an increase in the value of magnetic moment per Mn atom with increasing Cu composition. This may be attributed to the ferromagnetic ordering of the

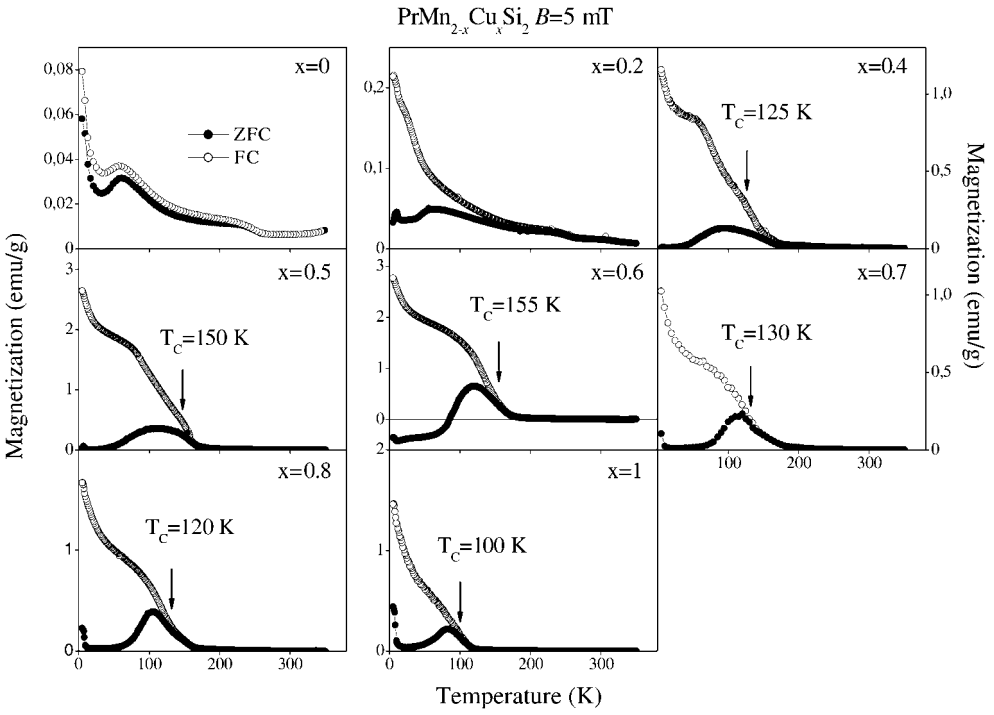

Figure 2. Temperature dependence of the magnetization of $PrMn_{2-x}Cu_xSi_2$ in the temperature range 5–350 K for an applied field of 5 mT. Open symbols refer to the field-cooled mode (FC), filled symbols refer to the zero-field cooled (ZFC).

Pr sublattice. A detailed neutron diffraction study is required to determine the exact origin and contributions to the total bulk moment. It is worth noting that Pr orders in $PrFe_2Si_2$ and a large reduction of the Pr moment is observed (1.41 μ_B versus about 2.75 μ_B in $PrFe_2Ge_2$) [9] with an ordering temperature of 7.7 K versus 14.2 K for $PrFe_2Ge_2$. In both cases, the *c* axis is the easy direction of the Pr moments. This result could be explained in the frame of a crystal field model which shows that the magnetic moment value depends critically on the higher order magnetocrystalline anisotropy parameters [9].

Further evidence for the magnetic ordering of the Pr sublattice is given by the Mn sublattice, as in general the ordering of the rare-earth sublattice at low temperatures reconfigures the arrangement in the Mn sublattice in RMn_2X_2. This is mainly related to the R–Mn couplings. Iwata *et al* [10] showed that for light rare earths the ferromagnetic coupling between the R and Mn sublattices is dominant. For example, in $NdMn_2Si_2$, the ferromagnetic Mn planes are ordered antiparallel along the *c* axis below 381 K [6]. A ferromagnetic ordering of the Nd sublattice occurs at 33 K and yields the spin reorientation phenomenon, so that the magnetic coupling between the two sublattices is mainly ferromagnetic with the easy axis parallel to the *c* axis. According to this general behaviour, the increases in $M(T)$ for $PrMn_{2-x}Cu_xSi_2$ with $x \geqslant 0.4$ can also be attributed to the ordering of the Pr sublattice below the Curie temperatures. The ordering of the Pr sublattice causes the Mn sublattice to order parallel along the *c* axis, so that ferromagnetic Mn planes begin to align parallel to the Pr sublattice. Finally, the ferromagnetic state becomes stable along the *c* axis. The present results are by no means conclusive, and further neutron diffraction studies are required to reveal the magnetic ordering of the Pr and Mn sublattices.

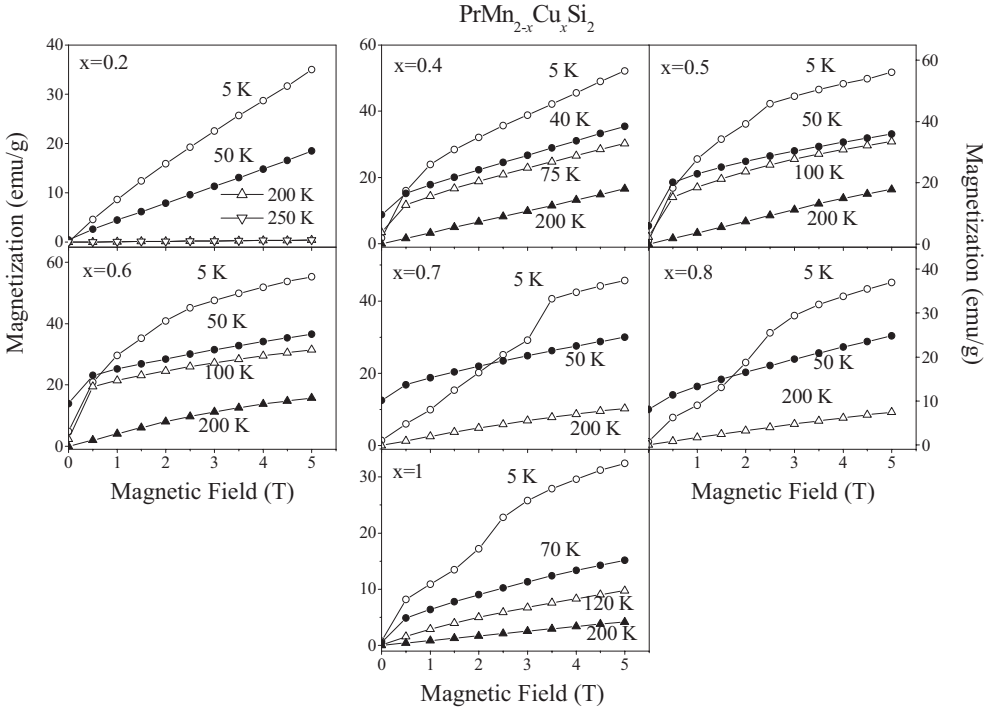

Figure 3. Magnetization as a function of applied field for $x = 0.2$, 0.4, 0.5, 0.6, 0.7, 0.8 and 1 at various temperatures.

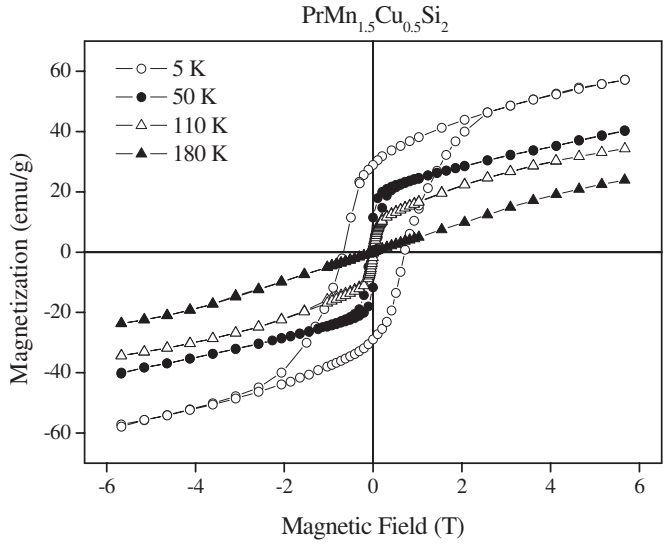

Figure 4. Hysteresis loops for the $x = 0.5$ compound at 5, 50, 110 and 180 K.

The magnetization curves for samples with $0.4 \leqslant x \leqslant 0.6$ are also similar in a sense that they exhibit similar features which shift gradually to higher temperatures with increasing Cu content. The transition temperatures of all samples are shown in figure 2. It is well known that in the 4f–3d compounds the Curie temperature is mainly determined by 3d–

3d interaction [11]. With increasing Cu content, the Curie temperature T_C increases from 125 K up to 155 K, but decreases again for samples with $x = 0.7, 0.8$ and 1. A similar increase of the Curie temperature was also observed in $GdMn_{1.5}Cu_{0.5}Ge_2$, $TbMn_{1.5}Cu_{0.5}Ge_2$ [12] and $NdMn_{2-x}Cu_xSi_2$ [13]. It is known that the RMn_2X_2 (X: Si or Ge) compounds have various magnetic structures, and various magnetic phase transitions are introduced by changing the temperature. These magnetic structures and transitions are related to the different types of exchange interactions, with different mechanisms contributing to them (the RKKY exchange interaction via conduction electrons on one hand, and superexchange between magnetic atoms via X atoms on the other). Generally, the exchange interactions in the RMn_2X_2 compounds can be divided into four classes: Mn–Mn in the layer, interlayer Mn–Mn, Mn–R and R–R [14]. Numerous studies have shown that the exchange interaction between Mn atoms in the layer is the strongest. This exchange interaction mainly determines the magnetic ordering temperature of the RMn_2X_2 compounds. The Mn–R exchange interaction has approximately the same value as the exchange interaction between nearest Mn planes. The competition of these two interactions determines the magnetic properties of these compounds at low temperatures. In the $PrMn_{2-x}Cu_xSi_2$ system, the substitution of Cu for Mn leads to an increase on the lattice constant a and decrease on the lattice constant c. This increase and decrease, respectively, result in an elongation of the Mn–Mn distance on one hand and a contraction of the Mn–Pr distance on the other. The contraction of the Mn–Pr distance might lead to the ordering of the Pr sublattice at higher temperatures, so that the stability range for the ferromagnetic arrangement becomes broader with respect to temperature for increasing Cu content. For the samples with $x = 0.7$, 0.8 and 1, the substitution of Cu for Mn weakens the molecular field produced by the Mn sublattice and this leads to the decreasing Curie temperature for these compounds. However, details of the competing magnetic interactions of the 3d subsystem in intermetallides of the RT_2X_2 type are not fully understood yet.

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