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Neutron diffraction study of the $La_{1-x}Pr_xMn_2Si_2$ ($x = 0.4$, 0.7 and 1) compounds and the general description of the magnetic behavior of Mn in RMn_2Ge_2 and RMn_2Si_2

I. Dincer[a,*], Y. Elerman[a], A. Elmali[a], H. Ehrenberg[b], G. André[c]

[a]Department of Engineering Physics, Faculty of Engineering, Ankara University, 06100 Besevler-Ankara, Turkey
[b]Institute for Materials Science, Darmstadt University of Technology, Petersenstrasse 23, D-64287 Darmstadt, Germany
[c]Laboratoire Léon Brillouin (CEA-CNRS), CEN-Saclay, 91191 Gif-Sur-Yvette, France

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Abstract

The magnetic structures of the $La_{1-x}Pr_xMn_2Si_2$ ($x = 0.4$, 0.7 and 1) have been investigated by powder neutron diffraction between 2 and 308 K. According to magnetic measurements, the $x = 0.4$ sample shows a typical $SmMn_2Ge_2$-like magnetic behavior. Neutron diffraction indicates a canted antiferromagnetic structure below 130 K and a canted ferromagnetic structure above 240 K. Between 130 and 240 K, the canted ferromagnetic and antiferromagnetic structures coexist. Since the magnetic moments of Mn atoms, the unit cell parameters and the scale parameters of the canted antiferromagnetism and canted ferromagnetism are highly correlated between 130 and 240 K, a special refinement procedure was introduced. The critical Mn–Mn value was determined as 2.87 Å, and the spontaneous volume change and linear magnetostriction are derived. Neutron diffraction revealed a canted antiferromagnetic structure for $La_{0.3}Pr_{0.7}Mn_2Si_2$. A canted antiferromagnetic structure was also detected for $PrMn_2Si_2$ by neutron diffraction in contrast to previous reports of a collinear arrangement. The present results are compiled together with previous ones on RMn_2Ge_2 and RMn_2Si_2 (R: Y, La and rare-earth) compounds in two magnetic phase diagrams. These two graphics summarize the general magnetic behavior of Mn in the RMn_2Ge_2 and RMn_2Si_2 compounds.

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Keywords: Magnetic measurements; Magnetic structures; Neutron diffraction; Magnetic phase diagram

1. Introduction

The ternary compounds RT_2X_2, where R is a rare-earth, T is a transition metal and X is Si or Ge, are of considerable interest due to a wide variety of phenomena, ranging from heavy fermion behavior and superconductivity to strong ferromagnetism and antiferromagnetism [1–8]. These compounds crystallize in the body-centered tetragonal TCr_2Si_2-type structure (space group I4/mmm), atoms are stacked in square layers perpendicular to the *c*-axis following the sequence R–X–T–X–R- [9].

The RMn_2X_2 compounds are of particular interest because Mn atoms carry a magnetic moment. The high sensitivity of exchange parameters to the intralayer Mn–Mn spacing governed by the lattice parameter *a* leads to complex and very interesting magnetic phase diagrams of these compounds. A number of studies have given an overview of the magnetic structures of RMn_2X_2, $R_{1-x}R'_xMn_2X_2$ and the magnetic properties, which are related to the Mn–Mn separation d^a_{Mn-Mn} [2,7,8,10–17]. Roughly, if $d^a_{Mn-Mn} > 2.87$ Å ($a > 4.06$ Å), the *intra*layer *in*-plane coupling is antiferromagnetic and the *inter*layer coupling is ferromagnetic. When $2.84\,\text{Å} < d^a_{Mn-Mn} < 2.87\,\text{Å}$ ($4.02\,\text{Å} < a < 4.06\,\text{Å}$), the *intra*layer *in*-plane coupling remains antiferromagnetic, but the *inter*layer coupling is also

*Corresponding author. Tel.: +90 312 212 6720; fax: +90 312 212 7343.
E-mail address: idincer@eng.ankara.edu.tr (I. Dincer).

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antiferromagnetic. In the case $d^a_{Mn-Mn} < 2.84$ Å ($a < 4.02$ Å),there is effectively no *intra*layer *in*-plane spin component, and the *inter*layer coupling remains antiferromagnetic.

Ijjaali et al. [14] and Hofmann et al. [15] investigated the magnetic structure and properties of the $La_{0.8}Y_{0.2}Mn_2Si_2$ compound which exhibits a typical $SmMn_2Ge_2$-like magnetic behavior by magnetic measurements and powder neutron diffraction. Since the canted antiferromagnetism and ferromagnetism coexist above T_N^{inter} up to T_C^{inter} in this compound, the transitions from the canted antiferromagnetism to ferromagnetism progresses over a broader temperature range. In some cases, the magnetic state in this range is denoted as an intermediate phase [18,19]. To determine magnetic structures, the values of magnetic moments and the unit cell parameters of both structures, special refinement procedures are mandatory in this temperature range. Hofmann et al. [15] have used a special refinement procedure. But this procedure is not sufficient, since they assume that both magnetic structures have the same value of the magnetic moment of Mn and the same canting angle with respect to the *c*-axis. However, the canting angle of the Mn magnetic moment should be different for the canted antiferromagnetic and ferromagnetic structures. In order to clarify whether both magnetic structures have different canting angles, a sample is requested which shows single canted ferromagnetic properties above T_N^{inter} up to T_C^{inter}. The $La_{1-x}Pr_xMn_2Si_2$ compounds exhibit a sharp transition from ferromagnetism to antiferromagnetism with decreasing temperature [20]. Because of this sharp transition, the neutron diffraction study of the $La_{1-x}Pr_xMn_2Si_2$ compounds will be interesting and provide more information about the magnetic structures above T_N^{inter} up to T_C^{inter}. In this work, an investigation on the magnetic structures of the $La_{1-x}Pr_xMn_2Si_2$ ($x = 0.4$, 0.7 and 1) compounds is reported. Furthermore our new and earlier results are combined into generalized phase diagrams to elucidate the systematics in the relationship between magnetic properties and underlying crystal structures for the RMn_2Ge_2 andRMn_2Si_2 compounds.

2. Experimental

The method for sample preparation by standard arc melting under purified argon (La and Pr 99.9%; Mn 99.98%; Si 99.999%) is described elsewhere [20]. The starting materials contained 3% excess Mn to compensate for the Mn loss due to evaporation during melting, and the ingot was melted five times for improved homogeneity. As our argon arc furnace can only load relatively small charges ~2 g, the samples for neutron diffraction experiments consisted of a mixture of fine powders from five ingots.

Each sample was checked for purity by powder X-ray diffraction on a Siemens D-500 using CuKα radiation and a secondary pyrolytic graphite (0 0 2) monochromator. Magnetization measurements in the temperature range $5\,K < T < 350\,K$ and in 50 Oe were carried out in a superconducting quantum interference device magnetometer (SQUID). The samples were first taken to a temperature above 350 K and then measured in a zero-field-cooled (ZFC) field-cooled (FC) sequence. Above room temperature, magnetization measurements were performed using a vibrating sample magnetometer (VSM) in an external magnetic field of 5 kOe, and measurements were taken both on increasing and decreasing temperature.

The powder neutron diffraction patterns were recorded on the diffractometer G 4.1 at the Laboratoire Léon Brillouin (LLB) in Saclay, France, at a wavelength of $\lambda = 2.42$ Å. Diffraction patterns were collected from $2\theta = 16^\circ$ to 96° in steps of 0.1° over the temperature range 2–308 K. The neutron patterns were analyzed with the Rietveld method using the program FULLPROF [21], allowing the simultaneous refinement of structural and magnetic parameters. Scale factor, background, lattice parameters, a position parameters z_{Si}, one common isotropic thermal displacement parameter for all sites and the magnetic moments of Mn were refined.

3. Results

3.1. Crystallographic data

The room temperature X-ray diffraction patterns for the $La_{1-x}Pr_xMn_2Si_2$ ($x = 0.4$, 0.7 and 1) compounds show the characteristic reflections of the body centered tetragonal $ThCr_2Si_2$-type structure. The refined lattice parameters *a* and *c*, c/a, the unit cell volume *V* and the *intra*layer Mn–Mn spacing d^a_{Mn-Mn} are listed in Table 1. The substitution of La with Pr leads to a decrease of the lattice constant with increasing *x*. The decrease is related to the smaller atomic size of Pr compared with La.

3.2. Magnetic measurements

The susceptibility measurements in the temperature interval 300–600 K in an applied field of 5 kOe were performed to determine the Néel temperature T_N^{intra} of *intra*layer Mn alignment (see Fig. 1). The Néel temperature T_N^{intra} is found to be 415, 430 and 450 K for the compounds with $x = 0.4$, 0.7 and 1, respectively. The Néel temperatures T_N^{intra} are derived from a change in slope of the inverse susceptibility of these compounds. The Néel temperatures T_N^{intra} are indicated by arrows in Fig. 1.

The results of the magnetization measurements in the temperature range 5–350 K for the $La_{1-x}Pr_xMn_2Si_2$ ($x = 0.4$, 0.7 and 1) compounds are given in Fig. 2. Below $T_C^{inter} = 296$ K, the $x = 0.4$ compound shows ferromagnetic properties. With decreasing temperature, the magnetization decreases just below 185 K, which indicates antiferromagnetic properties below this temperature. Ferromagnetic exchange is counteracted by antiferromagnetic exchange already just below the maximum in $M(T)$. However, antiferromagnetic ordering is not complete until the