Solid State Communications, Vol. 39, pp. 863–866.
Pergamon Press Ltd. 1981. Printed in Great Britain.

0038–1098/81/310863–04$02.00/0

# CRYSTALS AND MAGNETIC STRUCTURE OF $R\mathrm{Mn_2Si_2}$ ($R$ = Pr, Nd, Y) AND $\mathrm{YMn_2Ge_2}$

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(*Received* 2 *March* 1981 *by E. F. Bertaut*)

Crystallographic and magnetic properties of $\mathrm{PrMn_2Si_2}$, $\mathrm{NdMn_2Si_2}$, $\mathrm{YMn_2Si_2}$ and $\mathrm{YMn_2Ge_2}$ intermetallics were studied by X-ray, neutron diffraction and magnetometric measurements. The crystal structure of all four compounds was confirmed to be body-centered tetragonal (space group $I4/mmm$). All were found to be antiferromagnetic with Néel points at 368, 380, 460 and 395 K respectively. Neutron diffraction results indicate that their magnetic structure consists of ferromagnetic layers composed of Mn ions piled up along the $c$-axis. Each layer is antiferromagnetically coupled to adjacent layer. The magnetic space group is $I_p4/m'm'm'$. No magnetic ordering of the $R$ sublattice was observed at 1.8 K in the case of $R$ = Pr and Nd.

## 1. INTRODUCTION

INTERMETALLIC COMPOUNDS represented by the formula $RM_2X_2$ (where $R$ is a rare earth or actinide metal, $M$ is a transition 3$d$ or 4$d$ metal, $X$ is germanium or silicon) crystallize in the body-centered tetragonal structure: space group $D_{4h}^{17}$–$I4/mmm$. The $R$, $M$ and $X$ atoms occupy the 2(a), 4(d) and 4(e) positions respectively. The structure can be described as a stacking of atomic layers in the direction of $c$-axis. The sequence is $R$–$X$–$M$–$X$–$R$.

Previous studies indicate that in majority of these compounds, the $M$ metal (except Mn) carries no magnetic moment. On the other hand $R$ atoms usually order antiferromagnetically at low temperatures.

Magnetic studies show that $R\mathrm{Mn_2Si_2}$ compounds are either ferromagnetic or antiferromagnetic [1–4]. $\mathrm{CeMn_2Si_2}$ [3]. $\mathrm{ThMn_2Si_2}$ and $\mathrm{ThMn_2Ge_2}$ [4] were found to be collinear antiferromagnets. Magnetic ordering scheme consists of a sequence of ferromagnetic layers built of Mn atoms, stacked along the $c$-direction. Magnetic moment of Mn amounting to 2 $\mu_B$ at 80 K is aligned along the tetragonal axis. Narasimhan *et al.* [1] reported that $R\mathrm{Mn_2Ge_2}$ intermetallics (where $R$ = La, Ce, Pr and Nd) are ferromagnetic with Curie temperatures above 300 K. The easy axis of magnetization was found to be along the $c$-axis in all cases. On the other hand $\mathrm{NdMn_2Si_2}$ was found to be antiferromagnetic with Néel point at 380 K. At 32 K a sudden drop in magnetization was observed. To explain this behaviour Narasimhan [1] proposed the following models of magnetic ordering:

– at higher temperatures the Mn lattice is ordered antiferromagnetically but the Nd sublattice remains magnetically disordered

– at low temperatures the Nd sublattice is ordered and coupled ferromagnetically to the Mn sublattice.

Narasimhan *et al.* [1] reported also that $\mathrm{PrMn_2Si_2}$ exhibits at 4.2 K a linear increase of magnetization as function of applied field.

We report in this paper the results of X-ray, neutron diffraction and magnetrometric measurements performed on polycrystalline samples of $\mathrm{PrMn_2Si_2}$, $\mathrm{NdMn_2Si_2}$, $\mathrm{YMn_2Si_2}$ and $\mathrm{YMn_2Ge_2}$. The aim of this study is to determine their crystal structure and magnetic ordering scheme and to contribute in this way to the understanding of the magnetic properties of $RM_2X_2$ intermetallics.

## 2. EXPERIMENTAL AND RESULTS

The samples were synthetized by melting corresponding rare-earth metal or itrium (4$N$), mangenese (4$N$), silicon or germanium (5$N$ purity) in an induction furnace. The samples were annealed in a quartz tube at about 1100K for 100 h and cooled to room temperature.

The single-phase nature of the samples was checked by X-rays using Fe$K_\alpha$ radiation. All the lines observed could be indexed as due to tetragonal $\mathrm{ThCr_2Si_2}$-type structure.

Magnetometric measurements were carried out in the temperature range from 4.2 to 600 K using an electronic balance with a maximum field of 1 T.

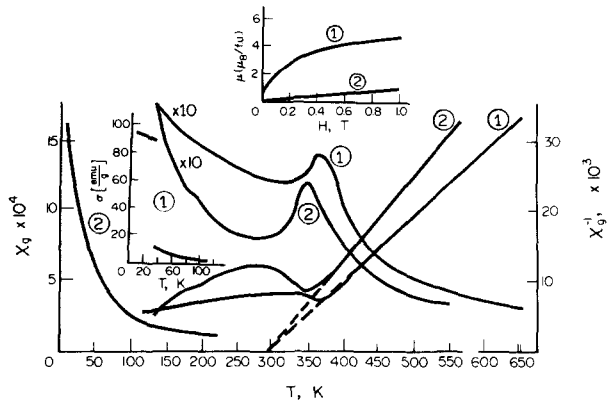



Fig. 1. Magnetic susceptibility against temperature dependence for 1, $PrMn_2Si_2$ and 2, $NdMn_2Si_2$.

The thermal variation of magnetic susceptibility exhibits a maximum (see Fig. 1) which is characteristic for antiferromagnetic behaviour below the Néel points of 348, 365, 460 and 395 K for $PrMn_2Si_2$, $NdMn_2Si_2$, $YMn_2Si_2$ and $YMn_2Ge_2$ respectively. In addition for $PrMn_2Si_2$ a strong increase in susceptibility is observed at low temperatures. In the case of $NdMn_2Si_2$ a sudden drop of magnetization was found at 32 K (see inset in Fig. 1).

In all compounds studied the reciprocal susceptibility obeys Curie–Weiss law at high temperatures. The positive asymptotic $\theta_p$ (paramagnetic temperatures) observed in all four samples suggest that the antiferromagnetic coupling is relatively weak, while the ferromagnetic interactions are fairly strong. Similar behaviour was observed in other layered structures. The magnetic data are collected in Table 1.

*Table 1. Magnetic characteristics of* $RMn_2X_2$ *compounds*

| Compound | $T_N$ (K) | $\theta$ (K) | $\mu_{eff}$ ($\mu_B$ mole$^{-1}$) |
|---|---|---|---|
| $PrMn_2Si_2$ | 348 | 290 | 5.1 |
| $NdMn_2Si_2$ | 365 | 290 | 5.1 |
| $YMn_2Si_2$ | 460 | 385 | 3.5 |
| $YMn_2Ge_2$ | 395 | 385 | 3.8 |

Neutron diffraction data were obtained using neutron powder diffractometre DN-500 at Świek reactor EWA. Neutron diffraction patterns were taken: for $PrMn_2Si_2$ at 1.8, 4.2, 100 and 293 K, for $NdMn_2Si_2$ at 1.8, 4.2, 150 and 293 K, for $YMn_2Si_2$ and $YMn_2Ge_2$ at 80 and 293 K.

All the reflections observed were indexable on the basis of the tetragonal unit cell determined earlier by X-rays. Refinement of the nuclear and magnetic data was performed using line profile analysis of Rietveld [5].

Nuclear intensities were calculated using the following atomic positions in the space group $I4/mmm$:

$R$ atoms in 2($a$): $0, 0, 0; \frac{1}{2}, \frac{1}{2}, \frac{1}{2}$;

Mn atoms in 4($d$) $0, \frac{1}{2}, \frac{1}{4}; \frac{1}{2}, 0, \frac{1}{4}; 0, \frac{1}{2}, \frac{3}{4}; \frac{1}{2}, 0, \frac{3}{4}$;

Si atoms in 4($e$): $0, 0, z; 0, 0, \bar{z}; \frac{1}{2}, \frac{1}{2}, \frac{1}{2} + z$; $\frac{1}{2}, \frac{1}{2}, \frac{1}{2} - z$;

Two possible atomic distributions were considered:

(1) (Nd, Pr), Mn, Si as above;
(2) (Nd, Pr), $(1-e)$ Mn + $e$ Si, $(1-e)$ Si + $e$ Mn,

i.e. allowing for the possibility of mixing the Mn and Si atoms among 4($d$) and 4($e$) sites. Free parameter $z$ and Debye–Waller temperature factors were determined from nuclear reflections by line profile refinement-method [5] using the scattering lengths of 0.44, 0.72, −0.39, 0.42, (all in $10^{-14}$ m) for Pr, Nd, Mn, Si, Y and Ge respectively [6]. Refined parameters and corresponding $R$-factors are listed in Table 2. Our experiment did not confirm the mixing of Mn and Si atoms between 4($d$) and 4($e$) sites.

Two superlattice lines of magnetic origin were observed on neutron-diffraction patterns obtained at 4.2 and 100 K. They were indexed as (1 1 1) and (1 1 3) basing on the crystallographic unit cell. Similar reflections were observed earlier on neutron-diffraction patterns of $CeMn_2Si_2$ [3], $ThMn_2Si_2$ and $ThMn_2Ge_2$ [4]. We have analysed the observed magnetic reflections assuming a collinear magnetic ordering scheme consisting of ferromagnetic layers composed of Mn atoms exhibiting $+-+-$ sequence along the $c$-axis. The absence of (00$l$) reflections indicates that magnetic moments are parallel to the fourfold axis. The values of magnetic moments are listed in Table 2. $Mn^{2+}$ form factor was assumed [7].

For $PrMn_2Si_2$ and $NdMn_2Si_2$ neutron-diffraction patterns taken at LHT are similar to those obtained at LNT. In the case of $PrMn_2Si_2$ this result confirms the magnetometric data showing that magnetic moments on Pr sublattice are not ordered at low temperatures. In the case of $NdMn_2Si_2$ neutron diffraction results are in contradiction to the results of magnetometric measurements which indicate the presence of spontaneous magnetisation at low temperatures. However any magnetic ordering of Nd sublattice should reflect itself in the observed neutron intensities (see Table 3). The magnetic contributions given in Table 3 were calculated assuming ferromagnetic ordering of $Nd^{3+}$ ions ($\mu = gJ = 3.28\mu_B$). The calculations were carried out for two models with:

– magnetic moments along the $c$-axis;
– magnetic moments perpendicular to the $c$-axis.

Since such an increase was not observed, the above models must be rejected. The only reasonable explanation is an assumption of antiferromagnetic ordering of

*Table 2. Structural and magnetic parameters in* $RMn_2Si_2$ (R = Pr, Nd, Y) *and* $YMn_2Ge_2$

| | $PrMn_2Si_2$ | | | | $NdMn_2Si_2$ | | | |
|---|---|---|---|---|---|---|---|---|
| $T$ (K) | 1.8 K | 4.2 K | 90 K | 293 K | 1.8 K | 4.2 K | 150 K | 293 K |
| $a$ (Å) | 4.024(9) | 4.020(11) | 4.024(4) | 4.030(3) | 4.043(7) | 4.054(9) | 4.061(7) | 4.063(4) |
| $c$ (Å) | 10.552(33) | 10.555(40) | 10.566(11) | 10.559(10) | 10.478(34) | 10.509(27) | 10.500(25) | 10.522(16) |
| $c/a$ | 2.622 | 2.626 | 2.626 | 2.670 | 2.592 | 2.592 | 2.586 | 2.590 |
| $V$ (Å$^3$) | 170.86(1.28) | 170.55(1.52) | 171.15(46) | 171.49(44) | 171.27(1.04) | 172.71(1.04) | 173.16(99) | 173.73(59) |
| $z$ | 0.381(4) | 0.382(6) | 0.383(2) | 0.375(2) | 0.369(1) | 0.365(1) | 0.365(3) | 0.358(2) |
| $R_N$ (%) | 6.9 | 6.1 | 5.6 | 8.3 | 6.0 | 4.6 | 6.2 | 6.5 |
| $\mu$ ($\mu_B$) | 2.48(12) | 2.45(16) | 1.96(10) | 0.85(23) | 2.57(18) | 2.57(18) | 2.46(14) | 1.32(20) |
| $R_m$ (%) | 12.9 | 13.1 | 12.5 | 15.7 | 7.8 | 9.5 | 10.2 | 16.5 |

| | $YMn_2Si_2$ | | $YMn_2Ge_2$ | |
|---|---|---|---|---|
| $T$ (K) | 80 K | 293 K | 80 K | 293 K |
| $a$ (Å) | 3.939(4) | 3.943(2) | 3.975(7) | 3.984(4) |
| $c$ (Å) | 10.501(15) | 10.510(10) | 10.763(26) | 10.850(14) |
| $c/a$ | 2.539 | 163.41(34) | 2.708 | 2.723 |
| $V$ (Å$^3$) | 162.92(46) | 2.665 | 170.11(95) | 172.21(45) |
| $z$ | 0.370(2) | 0.372(2) | 0.390(2) | 0.386(1) |
| $R_n$ (%) | 6.0 | 1.1 | 4.9 | 4.5 |
| $\mu$ ($\mu_B$) | 2.40(14) | 1.98(7) | 2.95(12) | 2.55(14) |
| $R_m$ (%) | 10.4 | 2.5 | 9.1 | 9.6 |

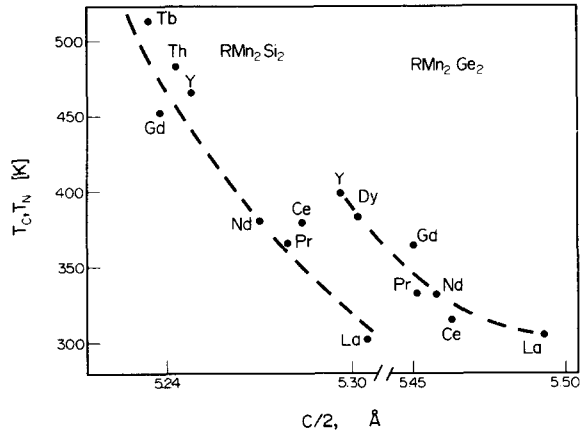
*Table 3. Calculated intensities of magnetic reflections in* $NdMn_2Si_2$. *Model 1: Magnetic moments* Nd *atoms parallel to* c*-axis. Model 2: Magnetic moments* Nd *atoms perpendicular to* c*-axis*

| | Model 1 | | Model 2 | |
|---|---|---|---|---|
| *hkl* | $I_m$ (barn) | $\frac{I_m}{I_n(110)}$(%) | $I_m$ (barn) | $\frac{I_m}{I_n(110)}$(%) |
| 002 | 0 | 0 | 187.48 | 22.28 |
| 101 | 331.73 | 39.4 | 215.7 | 25.63 |
| 110 | 105.2 | 12.5 | 52.6 | 6.25 |
| 103 | 80.25 | 9.5 | 145.7 | 17.3 |
| 004 | 0 | 0 | 44.1 | 5.2 |
| 112 | 124.54 | 14.8 | 98.8 | 11.7 |

Mn ions in zero magnetic field; However, it seems probable that already a very low external field induces at 32 K a metamagnetic transition. The above hypothesis seems to be supported by the data of Obermeyer *et al.* [8] who observed a distinct transition of this kind in Nd $(Mn_{1-x}Cr_x)_2Si_2$ solid solution.

## 3. DISCUSSION

The magnetic structures of $PrMn_2Si_2$, $NdMn_2Si_2$, $YMn_2Si_2$ and $YMn_2Ge_2$ are similar to those observed in $CeMn_2Si_2$ [3], $ThMn_2Si_2$ and $ThMn_2Ge_2$ [4]. Their layer-type crystal structure suggests the presence of magnetic interactions of strongly anisctropic character.



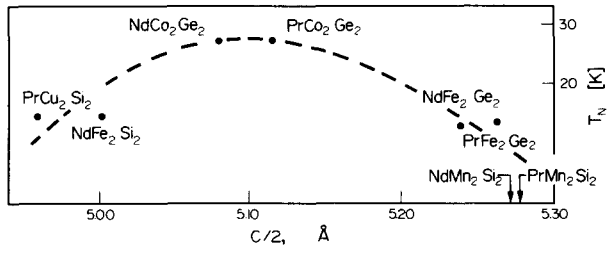




Fig. 2. (a, b) $M$–$M$ distances ($d_{M-M} = c/2$) and Néel (or Curie) points for a number of $RM_2X_2$ compounds.

Short Mn–Mn distance within the layer equal to $a\sqrt{2}/2$ prefers ferromagnetic ordering. This is consistent with the observed positive paramagnetic Curie temperatures, however, rather high magnetic transition temperatures

indicate that the interlayer interactions are not very weak. Figure. 2(a) presents interlayer distances in $R\mathrm{Mn_2Si_2}$ intermetallics. The values of Néel temperatures become smaller as the interlayer distances increase suggesting thus that the magnetic interactions are probably of superexchange type via two Si atoms. This follows directly from the comparison of the observed Mn–Si distance of 2.39 Å which is smaller than the sum of atomic radii $R_{\mathrm{Si}} + R_{\mathrm{Mn}} = 1.17 + 1.37 = 2.54$ Å indicating an overlap of electron shells. Consequently spin transfer from the $3p$ shell of Si to the $3d$ shell of Mn seems to be very probable resulting in a decrease of the magnetic moment on Mn atom.

It seems to be somewhat unexpected that the magnetic moments of Pr and Nd atoms in our samples do not order. Many $RM_2X_2$ intermetallic compounds are known to exhibit an antiferromagnetically ordered $R$ sublattice [9]. Low values of Néel temperatures of these compounds suggest that the dominant magnetic interaction is of the RKKY-type [10]. From Fig. 2(b) it follows, that the Néel points decrease with the increase of the interlayer distances. For samples studied by us the interlayer distances are 5.28 Å and 5.27 Å for $\mathrm{PrMn_2Si_2}$ and $\mathrm{NdMn_2Si_2}$ respectively. They are larger than those ones reported in [9] indicating that the Néel points of $\mathrm{PrMn_2Si_2}$ and $\mathrm{NdMn_2Si_2}$ are probably smaller than 1.8 K.

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