Journal of Alloys and Compounds, 185 (1992) 51–58
JALCOM 217

Ferromagnetic ordering of $NdNiSi_2$ and $PrNiSi_2$ studied by neutron diffraction and magnetic measurements

P. Schobinger-Papamantellos*
Institut für Kristallographie und Petrographie, ETHZ, CH-8092 Zürich (Switzerland)

K. H. J. Buschow
Philips Research Laboratories, 5600 JA Eindhoven (Netherlands)

(Received November 18, 1991)

Abstract

The magnetic properties of the compounds $PrNiSi_2$ and $NdNiSi_2$ were studied by means of magnetic measurements and neutron diffraction. Neutron diffraction experiments made in the paramagnetic regime confirmed the $CeNiSi_2$ structure reported earlier for these compounds. Refined atomic position parameters for both compounds are given. Neutron diffraction measurements performed in the magnetically ordered regime showed that the rare earth moments in $PrNiSi_2$ and $NdNiSi_2$ order ferromagnetically below $T_c = 20$ K and $T_c = 9.5$ K respectively. The preferred moment direction is along the c axis in both cases. Ferromagnetic ordering was also concluded from magnetic measurements performed on these compounds.

1. Introduction

Ternary compounds of the type $RMSi_2$ and $RMGe_2$ have been reported to exist for most rare earth elements R and for several transition metals M [1]. The crystal structure of these compounds is of the $CeNiSi_2$ type [2] which is closely related to the AlB_2 structure and the α-$ThSi_2$ structure. The proliferation of this class of ternary compounds makes it very suitable for studying the magnetic coupling between the rare earth moments and the effect of the transition metal component M on these couplings, the additional advantage being that the concentration of the M component can be varied within reasonable limits [1].

In a previous study we have investigated the magnetic properties of the compound $TbNiSi_2$ that was shown to order anti-ferromagnetically below $T_N = 36.2$ K [3]. In the present investigation we have focussed our attention to two compounds of the same series formed with light rare earth elements (R≡Pr and Nd).

*Permanent guest scientist at the Laboratory for Neutron Scattering, ETH, Zürich, c/o PSI, CH-5232 Villigen, Switzerland.

2. Experimental procedures and results

The $NdNiSi_2$ and $PrNiSi_2$ samples were prepared by arc melting from starting materials of at least 99.9% purity, followed by vacuum annealing at 800 °C for about 4 weeks. X-ray diffraction showed that after this treatment the samples were approximately single phase. All reflection lines were indexed on the basis of the orthorhombic $CeNiSi_2$ structure type [1].

The temperature dependence of the magnetization of $NdNiSi_2$ and $PrNiSi_2$ was studied by means of a SQUID magnetometer in the temperature range 4.2–350 K in magnetic field strengths up to 20 kOe. It may be seen from Fig. 1 that a strong increase in magnetization occurs around 20 K and 10 K for $PrNiSi_2$ and $NdNiSi_2$ respectively. The magnetization measured with $H=2$ T and 4.2 K corresponds to $2.1\mu_B$ and $1.7\mu_B$ for $PrNiSi_2$ and $NdNiSi_2$ respectively. In the range well above T_c the reciprocal susceptibility χ^{-1} behaves approximately according to the Curie–Weiss law with effective moments close to the free R^{3+} ion values.

The neutron diffraction data were obtained from $PrNiSi_2$ and $NdNiSi_2$ samples with the double-axis multicounter system at the Saphire Reactor, Würenlingen. The wavelength used for the data collection was $\lambda=0.170\ 59$ nm and the step increment of the diffraction angle 2θ was 0.10°. Measurements were made in the paramagnetic range as well as in the magnetically ordered range. All data were corrected for absorption and evaluated by means of the line profile analysis method [4, 5]. The scattering lengths and magnetic form factor used for the various elements are from ref. 6 and ref. 7 respectively.

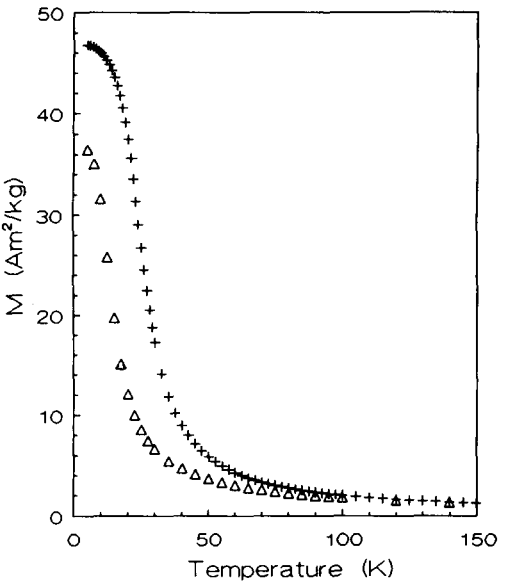

Fig. 1. Temperature dependence of the magnetization of $PrNiSi_2$ (+) and $NdNiSi_2$ (△).

Neutron diffraction powder data obtained in the paramagnetic state are shown in Figs. 2(a) and 3(a). These data confirm the $CeNiSi_2$ type of structure [1], adopted by all ternary rare earth (R) intermetallic disilicides RM_xSi_2 and digermanides where M is a transition metal of variable concentration. Refined parameters for $NdNiSi_2$ and $PrNiSi_2$ are given in Tables 1 and 2.

The low temperature neutron diffraction patterns (collected with the double counting rate rather than the nuclear data) are shown in Figs. 2(b)

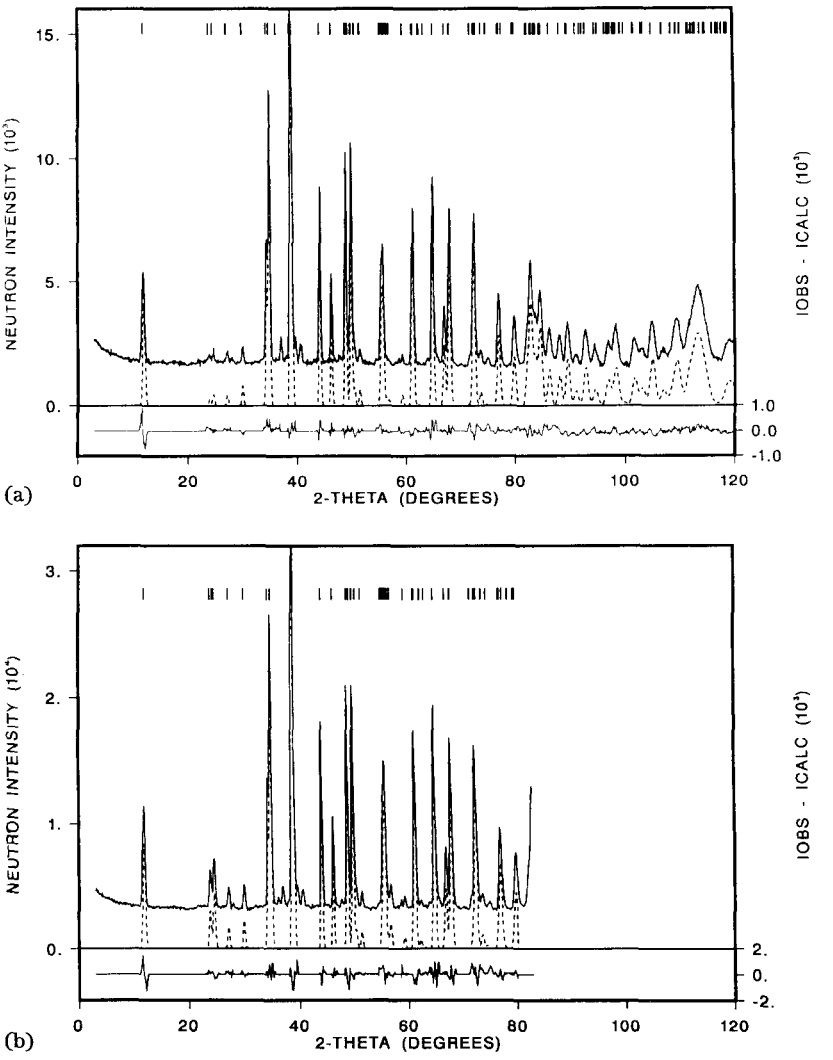

Fig. 2. (a) Neutron diffraction pattern of the compound $NdNiSi_2$ in the paramagnetic range (18 K; space group, *Cmcm*; 1.7008 A) and (b) data obtained in the magnetically ordered regime (1.5 K): ——, observed; – – –, calculated. The differences between observed intensities (corrected for background) and calculated intensities are plotted at the bottom of each part of the figure (right-hand scale).

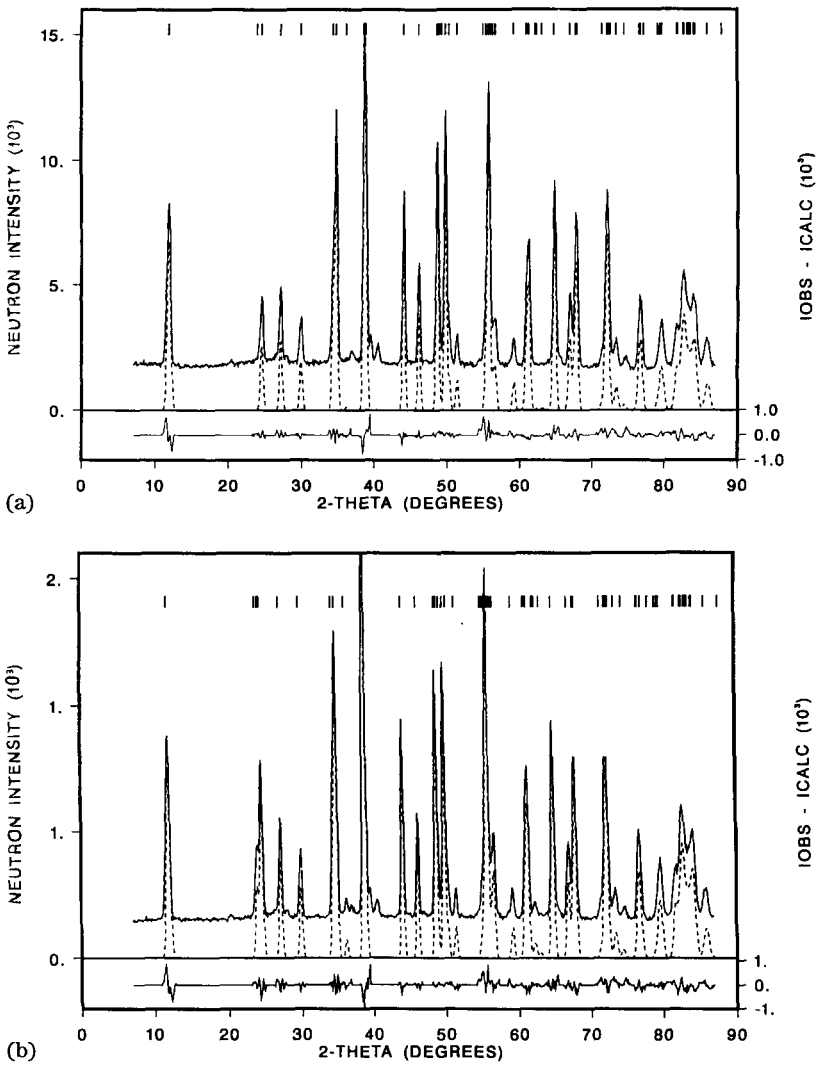

Fig. 3. (a) Neutron diffraction pattern of the compound $PrNiSi_2$ in the paramagnetic range (30 K; space group, *Cmcm*; 1.7012 A) and (b) data obtained in the magnetically ordered regime (9 K): ——, observed; – – –, calculated. The differences between observed intensities (corrected for background) and calculated intensities are plotted at the bottom of the figure (right-hand scale).

and 3(b). It may be inferred from these data that all magnetic reflections appear at reciprocal lattice positions of the chemical unit cell. The relative intensities of the first three observed magnetic reflections (020, 040 and 110) are shown in separate difference diagrams (Fig. 4). These data suggest that *b* cannot be the easy axis of magnetization and that the intensity enhancement is to be associated with ferromagnetic ordering in these compounds. This can be seen, for instance, from the observed intensity ratio

TABLE 1

Refined parameters for the neutron data of $NdNiSi_2$[a]

Parameter	Value	
	18 K	1.5 K
y (Nd)	0.1069(1)	0.1068(2)
y (Ni)	0.3195(1)	0.3197(2)
y (Si(1))	0.4592(3)	0.4601(6)
y (Si(2))	0.7500(3)	0.7507(5)
μ_z (μ_B)		2.38(5)
a (nm)	0.41144(2)	0.41128(3)
b (nm)	1.64343(10)	1.64282(15)
c (nm)	0.40361(2)	0.40337(3)
Overall temp. factor Bof (nm^2)	0.0026(2)	0.0004(1)
R_n, R_{wp}, R_m (%)	5.7, 10.6, –	3.0, 9.4, 9.5
R_{exp} (%)	3.9	2.1

[a]Space group *Cmcm* (No. 63); all atoms at 4c (0, y, 1/4).

TABLE 2

Refined parameters for the neutron data of $PrNiSi_2$[a]

Parameter	Value	
	30 K	9 K
y (Pr)	0.1069(1)	0.1073(3)
y (Ni)	0.3193(1)	0.3193(2)
y (Si(1))	0.4594(3)	0.4595(4)
y (Si(2))	0.7499(3)	0.7503(4)
μ_z (μ_B)		3.09(4)
a (nm)	0.41329(2)	0.41329(3)
b (nm)	1.64463(10)	1.64453(13)
c (nm)	0.40468(2)	0.40466(3)
Overall temp. factor Bof (nm^2)	0.0034(1)	0.0009(1)
R_n, R_{wp}, R_m (%)	4.8, 8.88, –	3.0, 8.5, 5.29
R_{exp} (%)	3.0	2.65

[a]Space group *Cmcm* (No. 63); all atoms at 4c (0, y, 1/4).

$I_0(020)/I_0(040)$ which is much smaller than unity. The calculated intensity ratio resulting from contributions of the real part of the structure factor only (ferromagnetic mode F + + + +) is 0.57, while the ratio resulting from the imaginary part (anti-ferromagnetic mode G + − + −) is 9.00. Evidently the former value compares more favourably with the experimental observations.

The refinement converged for magnetic moment directions along c for both compounds. The corresponding magnetic space group is *Cm'c'm* (Sh_{63}^{462}) which allows for the 4c symmetry position only an F_z ferromagnetic

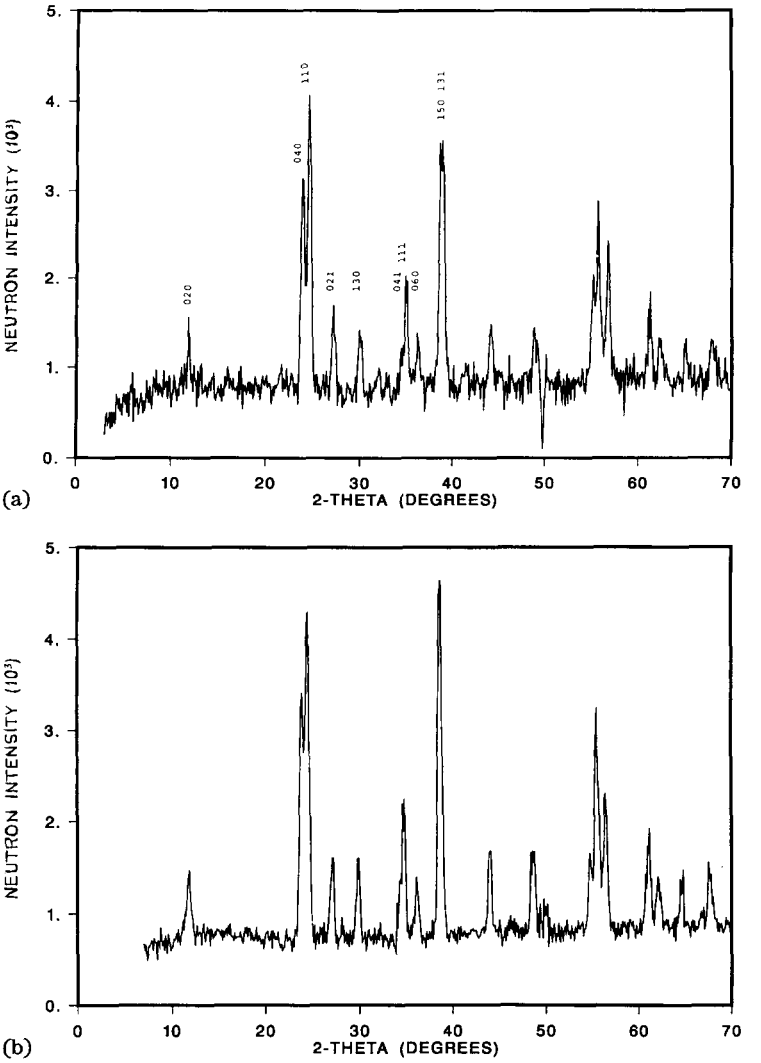

Fig. 4. Difference diagrams of (a) $NdNiSi_2$ and (b) $PrNiSi_2$ obtained by subtracting the nuclear contribution measured at the higher temperature in the paramagnetic regime from the intensities observed at the lower temperature in the magnetically ordered regime.

contribution. Apparently the axis of easy magnetization for the $RNiSi_2$ compounds formed of the light rare earths corresponds to the shortest axis c, as already found for the anti-ferromagnetic $TbNiSi_2$ in a recent investigation [3]. Refined parameters for $PrNiSi_2$ and $NdNiSi_2$ are listed in Tables 1 and 2. The R factors listed in Tables 1 and 2 indicate that there is a satisfactory agreement between observed and calculated moment arrangements. The magnetic R factor of the neodymium compound (9.5%) is higher than that of the praseodymium compound (5.29%). This is probably due to the presence of a small amount of an unidentified impurity phase in the former and the

lower value of the ordered moment ($2.38\mu_B$ for neodymium). The saturation moment of neodymium is below the value expected for the trivalent ion ($gJ = 3.27\mu_B$ for Nd^{3+}). In the case of $PrNiSi_2$ the saturation moment ($3.09\mu_B$) is much closer to the free trivalent ion value ($3.2\mu_B$ per praseodymium atom).

The moment values derived from neutron diffraction are substantially higher in both compounds than those derived from magnetic measurements. This may be due partly to the polycrystalline nature of the sample and the presence of magnetic anisotropy and partly to the fact that the magnetic ordering temperature is close to the lowest temperature considered in the magnetic measurements. The temperature dependence of the neutron intensity of two major reflection lines in both compounds is shown in Fig. 5. These results show that both compounds order ferromagnetically at quite different

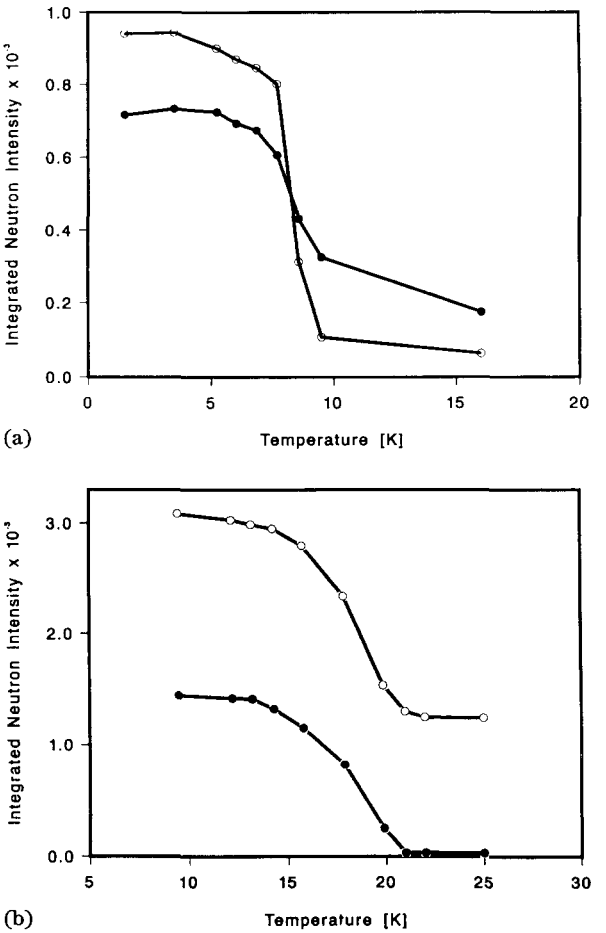

Fig. 5. Temperature dependence of the neutron intensities of two major reflection lines in (a) $NdNiSi_2$ and (b) $PrNiSi_2$: ○, (110); ●, (040).

temperatures, 9.5 K for $NdNiSi_2$ and 20 K for $PrNiSi_2$. The transition of the neodymium compounds displays a more abrupt character than that of $PrNiSi_2$.

3. Concluding remarks

It follows from the magnetic properties of the three $RNiSi_2$ compounds studied by us thus far (R≡Pr, Nd, Tb) that the magnetic coupling of the rare earth moments is of a complicated type. In the simplest case we expect that the coupling between the rare earth moments in metallic systems proceeds by means of the well-known conduction-electron-mediated RKKY coupling. This type of coupling can lead to ferromagnetism as well as to anti-ferromagnetism with the proviso that the type of coupling is preserved within a given series of rare earth compounds. Furthermore the Curie temperature varies as $(g-1)^2 J(J+1)$ in a given series of ferromagnetic compounds, meaning that the ordering temperature of the neodymium compounds is expected to be substantially higher than in the corresponding praseodymium compound. Both general rules are violated in $RNiSi_2$. This means that the type of coupling between the rare earth spin is not preserved when passing through this series of compounds. A study of the magnetic properties of other compounds of the $CeNiSi_2$-type structure is currently being undertaken.

References

1 M. Francois, G. Venturini, B. Malaman and B. Roques, *J. Less-Common Met.*, *160* (1990) 197, 215.
2 O. P. Bodak and E. I. Gladyshevskii, *Sov. Phys.—Crystallogr.*, *14* (1970) 859.
3 P. Schobinger-Papamantellos and K. H. J. Buschow, *J. Less-Common Met.*, *171* (1991) 321.
4 H. M. Rietveld, *J. Appl. Crystallogr.*, *2* (1969) 65.
5 A. W. Hewat, *Rep. AERE-R7350*, UK Atomic Energy Authority, Harwell, 1973.
6 V. Sears, in K. Skoeld and D. L. Price, *Methods of Experimental Physics 23A*, Academic Press, 1986, p. 521.
7 A. J. Freeman and I. P. Desclaux, *J. Magn. Magn. Mater.*, *12* (1979) 11.