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Magnetic ordering in $TbNiGe_2$ and $HoNi_{0.64}Ge_2$ by neutron diffraction

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Neutron diffraction measurements performed on polycrystalline samples of $TbNiGe_2$ and $HoNi_{0.64}Ge_2$ show that both exhibit at 4.2 K uniaxial antiferromagnetic ordering with G-mode. The magnetic moments of Tb and Ho are oriented parallel to the c-axis of a $CeNiSi_2$ type structure and at 4.2 K are $8.8\mu_B$ and $6.4\mu_B$ respectively.

1. Introduction

Among a number of phases occurring in the ternary systems composed of lanthanide elements (R), transition metals (T) and silicon, those taken in atomic ratio 1 : 1 : 2 with the $CeNiSi_2$ type of crystal structure [1], have recently attracted considerable attention, because they show interesting magnetic properties. Neutron diffraction studies have shown that $(Tb,Dy,Ho)CoSi_2$ [2], $TbNiSi_2$ [3] and $NdFeSi_2$ [4] order antiferromagnetically at low temperatures while $PrFeSi_2$ was found to behave as a ferromagnet [4]. The $CeNiSi_2$ type of crystal structure was also found to be common among ternary germanides [5,6]. Some of them were reported to order magnetically at low temperatures. Therefore we have undertaken a neutron diffraction study of the two compounds $TbNiGe_2$ and $HoNiGe_2$ which were reported to be antiferromagnets below 37 and 11 K, respectively [7].

2. Experiment

Both compounds were obtained by arc melting the respective elements (purity at least 3N) in an argon atmosphere. After melting and grinding the samples were sealed in quartz capsules and annealed for 7 days at a temperature of about 1100 K. X-ray powder patterns (Co K_α radiation) showed both samples to be single phase with

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crystal structure of CeNiSi$_2$ type. Neutron diffraction experiments were carried out at the Świerk reactor EWA. Diffraction patterns at 4.2 and 300 K were recorded using the DN500 powder diffractometer. The neutron wavelength was 1.324 or 1.563 Å. Data processing was performed by the Rietveldt method using nuclear scattering lengths from ref. [8] and the magnetic form factors of the respective R^{+3} ions taken from ref. [9].

3. Results

3.1. The crystal structure

The intensities of the nuclear reflections observed in the room temperature patterns were used for the refinement of the crystallographic parameters. The reflections were found to obey the extinction rule characteristic of the orthorhombic space group Cmcm. The intensities were calculated adopting the atomic positions of the CeNiSi$_2$ type structure i.e. the 4(c) site with the following coordinates: 0, y, 1/4; 0, $\bar{y}$, 3/4; 1/2, $1/2+y$, 1/4; 1/2, $1/2-y$, 3/4. The y parameter of each atom Tb (or Ho), Ni, GeI and GeII and the occupancy of nickel were subjected to a least squares refinement. While the occupancy of nickel in TbNiGe$_2$ was found to be almost 100%, the R factor in the case HoNiGe$_2$ was reduced from 20% to 7% for a nickel content of (64 ± 10)%. This means that the formula of HoNiGe$_2$ is in fact HoNi$_{0.64}$Ge$_2$. The lattice constants obtained, the values of y parameters and occupancy factors are collected together in table 1.

3.2. The magnetic structure

The neutron diffraction patterns of both compounds recorded at 4.2 K show a number of additional reflections of magnetic origin (fig. 1). They were indexed on a magnetic unit cell which has the same dimensions as the crystallographic one. The absence of the 001 magnetic reflection indicates that the magnetic moments are aligned along the short c-axis. The indices of the magnetic reflections indicate also the G-mode magnetic structure, the same as is found in HoCoSi$_2$ [10]. The moments located on planes with $z = 1/4$ and $z = 3/4$ are coupled ferromagnetically, while the coupling between adjacent planes is antiferromagnetic. The projection of this structure on the

Table 1
Crystal and magnetic data of TbNiGe$_2$ and HoNi$_{0.64}$Ge$_2$

	TbNiGe$_2$			HoNi$_{0.64}$Ge$_2$		
	RT [a]	RT [b]	LHT [b]	RT [a]	RT [b]	LHT [b]
a [Å]	4.096 (5)	4.095 (5)	4.118 (5)	4.084 (6)	4.095 (4)	4.094 (4)
b [Å]	16.67 (1)	16.681 (13)	16.399 (27)	16.29 (1)	16.286 (27)	16.283 (28)
c [Å]	4.086 (4)	4.077 (4)	4.041 (5)	4.019 (5)	4.030 (4)	4.024 (4)
V [Å^3]	278.99 (78)	278.49 (69)	272.91 (93)	267.38 (89)	268.74 (63)	268.25 (99)
N	0.94 (9)	1.00 (2)	1.00 (4)	0.71 (8)	0.64 (10)	0.64 (10)
y_R		0.1058 (9)	0.1050 (6)		0.1028 (6)	0.1053 (6)
y_{Ni}		0.3213 (5)	0.3167 (5)		0.3167 (4)	0.3111 (5)
y_{GeI}		0.4541 (7)	0.4508 (7)		0.4489 (7)	0.4508 (7)
y_{GeII}		0.7424 (8)	0.7482 (7)		0.7495 (7)	0.7490 (7)
R_n [%]		4.27	5.1		7.0	7.6
T_N [K]			37			11
μ [μ_B]			8.8 (1)			6.7 (1)
gJ			9.0			10.0
R_m (%)			7.3			8.64

[a] ref. [6].
[b] This work.

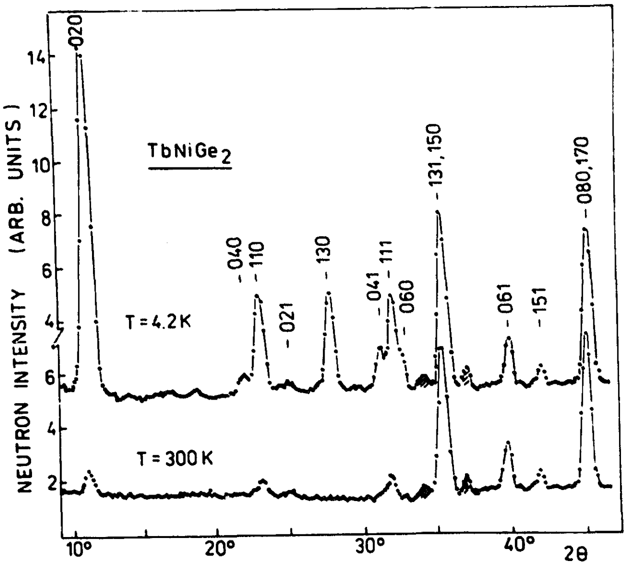

Fig. 1. Neutron diffraction patterns of $TbNiGe_2$ recorded at 4.2 and 300 K.

(100) plane is displayed in fig. 2. At 4.2 K magnetic moments of $(8.8 \pm 0.1)\mu_B$ and $(6.7 \pm 0.1)\mu_B$ are localized on Tb and Ho ions respectively, but no magnetic moment on nickel ion could be detected within the accuracy of our experiment. The magnetic data are listed in table 1.

4. Discussion

The crystal structure of $CeNiSi_2$ type can be schematically represented as a system of atomic planes stacked along the *b*-axis with the following sequence:

$$\cdots\text{-R-T-SiII-T-R-SiI-SiI-R-TSiII-T-R-}\cdots.$$

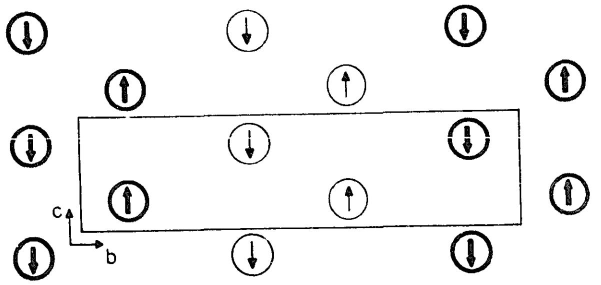

Fig. 2. The projection of the magnetic structure of $TbNiGe_2$ on the (100) plane. Only Tb ions are shown. The thick circles represent Tb ions at $x = 0$, the thin ones refer to $x = 1/2$.

Considering only the interatomic distances which indicate the occurrence of chemical interactions, the structure of $TbNiGe_2$ and $HoNi_{0.64}Ge_2$ can be visualized as a framework of slightly distorted square atoms at the apices and a nickel atom inside. The pyramids share common corners of GeII while the top corners of GeI atoms point up and down along the *b*-axis, giving rise to double layers. The five Ni–Ge distances in a pyramid range from 2.218 to 2.427 Å (mean 2.3357 Å). This value is close to 2.36 Å – the sum of the Pauling atomic radii of Ni and Ge corrected for the coordination number six. The double layers are interconnected by GeI–GeI bonds, 2.393 Å long. The network of Ge atoms constituting the pyramids appears to be very strong, since it does not break down, even when more than one half of the pyramids remains empty, as in $SmFe_{0.45}Ge_2$ [5]. In $HoNi_{0.64}Ge_2$ only two thirds of the pyramids contain a nickel atom inside. The Tb (or Ho) ions are located in tunnels expanding in the direction of the *c*-axis. Each R ion has ten Ge atoms as nearest neighbours at distances ranging from 3.050 to 3.259 Å (average 3.1357 Å) in the case of $TbNiGe_2$. This value compares well with the sum of the Pauling metallic radii of Tb and Ge for coordination number 12 amounting to 3.22 Å. $TbNiGe_2$ and $HoNi_{0.64}Ge_2$ exhibit a uniaxial antiferromagnetic structure of the same type as is found in $HoCoSi_2$ [10]. The Tb–Tb closest approach in $TbNiGe_2$ which amounts to 4.086 Å is long enough to exclude any direct magnetic interaction. Therefore the observed magnetic ordering scheme seems to be stabilized by long range interactions, probably those described by the RKKY model. The magnitudes of the magnetic moments determined at 4.2 K and localized on Tb^{+3} and Ho^{+3} ions are smaller than the free-ion values *gJ*. This may be result of strong crystal field anisotropy.

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