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Magnetism and magnetocaloric effect in YNi_4Si-type RNi_4Si (R=Ce, Gd, Tb and Dy) compounds

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ABSTRACT

Magnetic properties and magnetocaloric effect of YNi_4Si-type RNi_4Si (R=Ce, Gd, Tb and Dy) compounds have been investigated. Magnetic measurements indicate the intermediate valence state of cerium in YNi_4Si-type $CeNi_4Si$. The magnetocaloric effect of $GdNi_4Si$, $TbNi_4Si$ and $DyNi_4Si$ are calculated in terms of isothermal magnetic entropy change and they reach maximum values of −22.9 J/kg K, −13.5 J/kg K and −15.6 J/kg K for a field change of 140 kOe near ~28 K, 47 K and 27 K and they show maximum values of −12.7 J/kg K, −7.8 J/kg K and −9.3 J/kg K for a field change of 50 kOe near ~28 K, 42 K and 22 K, respectively. In contrast to $GdNi_4Si$, the magnetization-field isotherms for $TbNi_4Si$ and $DyNi_4Si$ exhibit hysteresis loop at 2 K due to strong magnetocrystalline anisotropy.

1. Introduction

Recently, an orthorhombic derivative of $CaCu_5$-type structure was detected in the YNi_4Si-type RNi_4Si compounds (R=Y, La, Ce, Sm, Gd–Ho) [1]. The YNi_4Si-type {Gd, Tb, Dy}Ni_4Si compounds show ferromagnetic-type ordering at 25 K, 37 K and 19 K, respectively. Below the magnetic ordering temperature, $TbNi_4Si$ exhibits the *b*-collinear magnetic ordering of Tb magnetic sublattice with **Cmm′m** magnetic space group and wave vector $\mathbf{K}=[0, 0, 0]$ (here $\mathbf{Cmm'm}=\{\mathbf{1}, \mathbf{m}_x, \mathbf{2}_y, \mathbf{m}_z\}\times\{\mathbf{1},\mathbf{1}'\times\mathbf{i}\}\times\{\mathbf{1}, \mathbf{1}/[1/2, 1/2, 0]\}$). The Tb magnetic moment reaches a value of 8.66 μ_B/Tb in zero applied filed while no magnetic ordering was detected for Ni sublattice of $TbNi_4Si$ [1,2]. Perhaps, the orthorhombic distortion of initial $CaCu_5$-type compounds is a prospective way to optimize the magnetic properties [3,4]. For these reasons, the magnetic properties of YNi_4Si-type {Ce, Gd–Dy}Ni_4Si have been investigated in detail in the present work.

The valence state and magnetic properties of $CaCu_5$-type $CeNi_4Si$ [5] and magnetic properties and magnetocaloric effect of $CaCu_5$-type $GdNi_4Si$ [6] and $GdNi_5$[7] and magnetic properties of $DyNi_4Si$ [8] and {Tb, Dy}Ni_5[9,10] were investigated earlier. This work aims to understand some of the specific features of magnetic properties of the YNi_4Si-type RNi_4Si compounds as the orthorhombic derivatives of $CaCu_5$-type compounds.

2. Materials and methods

The RNi_4Si sample were prepared by arc-furnace melting of the stoichiometric amounts of Ce, Gd, Tb and Dy (99.9 wt%), Ni (99.95 wt%) and Si (99.99 wt%). The samples were annealed at 1070 K for 200 h in an argon atmosphere and subsequently quenched in ice-cold water. The structure, phase purity and composition of the polycrystalline samples were evaluated using powder X-ray diffraction (XRD) and electron microprobe analysis. The X-ray data were obtained on a Rigaku D/MAX-2500 diffractometer (Cu $K_{\alpha1}$ radiation, $2\theta=10$–80 °, step 0.02 °, 1 s per step). An INCA-Energy-350 X-ray EDS spectrometer (Oxford Instruments) on the Jeol JSM-6480LV scanning electron microscope (20 kV accelerating voltage, beam current 0.7 nA and beam diameter 50 μm) was employed to perform the microprobe analyzes of the samples. Signals averaged over three points per phase estimated standard deviations of 1 at% for rare earth elements (measured by L-series lines), 1 at% for Ni and 1 at% for Si (measured by K-series lines).

Magnetization measurements on polycrystalline samples were carried out using a vibrating sample magnetometer (VSM attachment on PPMS Dynacool System, Quantum Design, USA) in the temperature range of 2–300 K and in magnetic fields up to 140 kOe. Magnetization data were obtained in zero-field-cooled (zfc) and field-cooled (fc) states in 100 Oe applied field to determine the magnetic ordering temperatures. Magnetization as a function of temperature was measured in 5 kOe field in zero-field-cooled state to obtain effective paramagnetic moments and paramagnetic Curie temperatures. Magnetization-field hysteresis curve

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was recorded at 2 K to obtain saturation magnetic moments and coercive field data. Magnetization-field isotherms were obtained at various temperatures ranging from 2 K to 102 K with a temperature step of 5 K and a field step of 2.5 kOe to calculate isothermal magnetic entropy change near the magnetic transition.

The unit cell data were derived from powder XRD using the Rietan-program [11,12] in the isotropic approximation at room temperature. The paramagnetic susceptibility was fitted to Curie–Weiss law and the effective magnetic moments and paramagnetic Curie temperatures were obtained [13]. Magnetocaloric effect (MCE) is calculated in terms of the isothermal magnetic entropy change, ΔS_m, using the magnetization vs. field data obtained near the magnetic transition using the thermodynamic Maxwell equation [14].

3. Results

3.1. Crystal structure

Both microprobe and X-ray powder analyzes show that RNi$_4$Si (R=Ce, Gd, Tb and Dy) are single-phase samples with composition of ternary phase of $R_{16(1)}Ni_{68(1)}Si_{16(1)}$ having YNi$_4$Si-type structure (Table 1). As a rule, the formation of CaCu$_5$-type RNi$_4$Si solid solution leads to a small expansion of the unit cell along the c axis and an increase of unit cell volume V relative to that of the initial CaCu$_5$-type RNi$_5$ compounds. However, the formation of YNi$_4$Si-type RNi$_4$Si compounds leads to an expansion of the unit cell along the a axis, but a contraction along b and c axes with still an increase of the unit cell volume V relative to that of the initial unit cell of CaCu$_5$-type RNi$_5$ and RNi$_4$Si compound as shown in Table 1 (initial CaCu$_5$-type RNi$_5$ and RNi$_4$Si compounds are given in term of YNi$_4$Si-type structure in Table 1 for comparison).

3.2. CeNi$_4$Si

Magnetization and inverse magnetic susceptibility of YNi$_4$Si-type CeNi$_4$Si vs. temperature in an applied field of 5 kOe are shown in Fig. 1**a**. The experimental data were fitted with the modified Curie–Weiss law $\chi(T)=\chi_0+C/(T-\Theta_P)$. The obtained $\chi_0=5.84\times10^{-4}$ emu/mol, $\Theta_P=-4.8$ K and $C=2.9\times10^{-2}$ emu K/mol and the effective magnetic moment $M_{eff}=0.48$ μ$_B$/f.u. derived from the Curie constant C are close to that observed in CaCu$_5$-type CeNi$_4$Si [5] (Fig. 1b). Since, the magnetic moment of Ce^{4+} is zero (and Ce^{3+} ion value M_{eff}/Ce=2.54 μ$_B$[15]), the reduction of the moment in YNi$_4$Si-type CeNi$_4$Si down to $M_{eff}=0.48$ μ$_B$ may be due to the Ce intermediate-valence, as in CaCu$_5$-type CeNi$_4$Si with $M_{eff}=0.52$ μ$_B$/fu [5]. According to the magnetization data, the CeNi$_4$Si does not show magnetic ordering down to 2 K in an applied field of 5 kOe (Fig. 1a).

The ferromagnetic-like behavior in the M–H isotherm and a small value of magnetic moment of 0.04 μ$_B$/fu in 140 kOe at 2 K of YNi$_4$Si-type CeNi$_4$Si (Fig. 1c) is close to that observed in CaCu$_5$-type CeNi$_4$Si with $M_{sat}=0.05$ μ$_B$/fu in field of 90 kOe at 1.7 K [5].

Thus, the YNi$_4$Si-type CeNi$_4$Si also shows mixed valence of Ce^{3+}-Ce^{4+}, as in the CaCu$_5$-type CeNi$_4$Si [5].

3.3. GdNi$_4$Si.

The paramagnetic susceptibility of GdNi$_4$Si in the temperature range of ~30–300 K in 5 kOe field follows Curie–Weiss law (inset in Fig. 2a and b). The fit to the Curie–Weiss law yields a positive paramagnetic Weiss temperature $\Theta_p=24.7$ K and an effective magnetic moment per formula unit (M_{eff}/fu) of 8.12 μ$_B$ for GdNi$_4$Si. This M_{eff}/fu yields an effective magnetic moments per Ni of ~0.9 μ$_B$ in GdNi$_4$Si (assuming that Gd has the theoretical Gd^{3+} effective moment of 7.94 μ$_B$[15]) which is slightly more than the theoretical magnetic moment of pure Ni (0.616 μ$_B$) [15]. However, such effective magnetic moment M_{eff}/fu may be a result of a contribution from conduction electron polarization which increase the effective moment from free ion value without invoking the moment on Ni.

The low field zfc and fc magnetization data obtained in 100 Oe field indicate a ferromagnetic ordering at 26 K for the GdNi$_4$Si compound (Fig. 2a).

The saturation behavior of magnetization at 2 K and the value of magnetic moment of 7.2 μ$_B$/fu in 140 kOe field at 2 K suggests a collinearly ordered ferromagnetic state of GdNi$_4$Si (the theoretical ordered state moment of Gd^{3+} ion is 7 μ$_B$[15]) (Fig. 2b). In fields of ~10 kOe the magnetization of GdNi$_4$Si orders completely (Fig. 2c).

Table 1
Unit cell data of CaCu$_5$-type RNi$_5$ and RNi$_4$Si and YNi$_4$Si-type RNi$_4$Si compounds (R=Ce, Gd, Tb and Dy) (space group *Cmmm*, N 65, oC12). The unit cell of CaCu$_5$-type RNi$_5$ and RNi$_4$Si compounds are given in term of YNi$_4$Si-type unit cell.

N	Compound	Type structure	**a (nm)**	**b (nm)**	**c (nm)**[b]	y_{Ni1}	$3^{1/2}\bullet a/b$	**V (nm^3)**	Refs.
1	CeNi$_5$	CaCu$_5$	0.4874	0.84420	0.4004	1/3	1	0.164750	[17,18]
	CeNi$_4$Si	CaCu$_5$	0.4852	0.84039	0.40536	1/3	1	0.165289	[5]
	CeNi$_4$Si	YNi$_4$Si	0.50424	0.82018	0.40108	0.3379	1.06485	0.165874	[1]
2	GdNi$_5$	CaCu$_5$	0.4902	0.84905	0.3964	1/3	1	0.164984	[17,18]
	GdNi$_4$Si	CaCu$_5$	0.4904	0.84940	0.3977	1/3	1	0.165660	[6]
	GdNi$_4$Si	YNi$_4$Si	0.50769	0.82353	0.39525	0.3396	1.06778	0.165253	[1]
3	TbNi$_5$	CaCu$_5$	0.4894	0.84767	0.3966	1/3	1	0.164529	[17,18]
	TbNi$_4$Si	CaCu$_5$	…	…		1/3	1		[8]
	TbNi$_4$Si[a]	YNi$_4$Si	0.50626(1)	0.82189(1)	0.39516(1)	0.3396(2)	1.06689	0.164420	This work[1]
4	DyNi$_5$	CaCu$_5$	0.48756	0.84448	0.39673	1/3	1	0.163347	[17,18]
	DyNi$_4$Si	CaCu$_5$	…	…		1/3	1		[8]
	DyNi$_4$Si	YNi$_4$Si	0.50479	0.82005	0.39499	0.3415	1.06619	0.163505	[1]

[a] TbNi$_4$Si: Tb 2a, [0, 0, 0] Ni1 4i [0, y_{Ni}, 0], Ni2 4f [1/4, 1/4, 1/2], Si 2c [1/2, 0, 1/2], $\beta_{11}=0.009754$, $\beta_{22}=0.003701$, $\beta_{33}=0.016010$ ($\beta_{11}=[1\ [A]/2a]^2$, $\beta_{22}=[1\ [A]/2b]^2$, $\beta_{33}=[1\ [A]/2c]^2$), $R_F=2.7\%$. The crystallographic data of TbNi$_4$Si used with permission– JCPDS – International Center for Diffraction Data.

[b] Shortest $R-2R$ interatomic distance is same to the c cell parameter of the CaCu$_5$-type and YNi$_4$Si-type compound.