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Magnetic ordering in Sc_2CoSi_2-type R_2FeSi_2 (R=Gd, Tb) and R_2CoSi_2 (R=Y, Gd–Er) compounds

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ABSTRACT

Magnetic and magnetocaloric properties of Sc_2CoSi_2-type R_2TSi_2 (R=Gd–Er, T=Fe, Co) compounds have been studied using magnetization data. These indicate the presence of mixed ferromagnetic and antiferromagnetic interactions in these compounds. One observes a ferromagnetic transition followed by an antiferromagnetic order and a further possible spin-reorientation transition at low temperatures. Compared to $Gd_2\{Fe, Co\}Si_2$, the Tb_2FeSi_2 and $\{Tb–Er\}_2CoSi_2$ compounds exhibit remarkable hysteresis (for e.g. Tb_2FeSi_2 shows residual magnetization $M_{res}/Tb=2.45\ \mu_B$, coercive field $H_{coer}=14.9$ kOe, and critical field $H_{crit}\sim5$ kOe at 5 K) possibly due to the magnetocrystalline anisotropy of the rare earth. The $R_2\{Fe, Co\}Si_2$ show relatively small magnetocaloric effect (i.e. isothermal magnetic entropy change, ΔS_m) around the magnetic transition temperature: the maximal value of MCE is demonstrated by Ho_2CoSi_2 ($\Delta S_m=-8.1$ J/kg K at 72 K and $\Delta S_m=-9.4$ J/kg K at 23 K in field change of 50 kOe) and Er_2CoSi_2 ($\Delta S_m=-13.6$ J/kg K at 32 K and $\Delta S_m=-8.4$ J/kg K at 12 K in field change of 50 kOe).

1. Introduction

The $R_2\{Fe, Co\}Si_2$ (R=Sc, Y, Gd–Tm) crystallize in the monoclinic Sc_2CoSi_2-type structure (space group $C2/m$, N 12, $mS20$) [1–4], like the R_2CoGe_2 (R=Sc, Nd, Sm, Gd–Tm, Lu, [5,6]). R_2RuGe_2 (R=Y, La–Nd, Sm, Gd–Er) [7–9], Y_2RhSi_2 [10], R_2RhGe_2 (R=Nd [6], Sm [7], Ho [11]), Ho_2OsGe_2 [12] and R_2IrGe_2 (R=Nd [13], Ho [6], Yb [14]) compounds. The rare earth sublattice seems to influence the magnetic ordering of Sc_2CoSi_2-type compounds. This structural arrangement is an example of superposition of two independent positions for the rare earth (4i) (x, 0 z) sublattices and this structural arrangement in Sc_2CoSi_2-type compounds leads to the observed complex magnetism [1,2]. However, such complex magnetic ordering demands a more detailed investigation. Moreover, the magnetic properties of Sc_2CoSi_2-type compounds supplement the magnetic properties of rare earth compounds with general formula $R_2T_{3-x}X_x$ of hexagonal Gd_2Co_2I-type, monoclinic Tm_2Ge_3-type, orthorhombic Mn_2AlB_2-type, Mo_2NiB_2-type, Er_2Pd_2Si-type, La_2Ni_3-type, tetragonal Mo_2FeB_2-type structures [16, 17]. and others,

Recently, the magnetic properties of Gd_2CoSi_2 and Gd_2CoGe_2 were investigated in [15] via magnetic measurements and the magnetic ordering in R_2FeSi_2 and R_2CoSi_2 compounds (R=Y, Gd–Tm) was investigated via magnetic and electrical resistivity measurements in [1,2]. This work is rather a continuation of the earlier studies and the magnetic properties of R_2TSi_2 (R=Gd–Er, T=Fe, Co) compounds have been studied using detailed magnetization measurements.

2. Materials and methods

The $R_2\{Fe, Co\}Si_2$ samples (R=Y, Gd–Er) were prepared by arc-furnace melting of stoichiometric amounts of rare earth (99.9 wt%), Fe, Co (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

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Table 1
Unit cell data of Sc_2CoSi_2-type R_2FeSi_2 and R_2CoSi_2 compounds (R=Y, Gd–Er, space group $C2/m$, N 12, $mS20$).

Compound	a (nm)	b (nm)	c (nm)	β (deg)	V (nm^3)	R_F (%)	Ref.
Gd_2FeSi_2	1.0655	0.4174	1.0093	118.95	0.39279		[2]
Gd_2FeSi_2	1.06595(9)	0.41720(5)	1.00966(9)	118.973(8)	0.39282	5.7	[a]
Tb_2FeSi_2	1.0564	0.4151	1.0014	118.84	0.38466		[2]
Tb_2FeSi_2[b]	1.05649(9)	0.41533(4)	1.00149(9)	118.847(6)	0.38492	5.4	[a]
Y_2CoSi_2	1.0409	0.4144	0.9993	118.64	0.37831		[3]
Y_2CoSi_2[c]	1.03991(9)	0.41452(4)	0.99897(9)	118.637(7)	0.37794	5.1	[a]
Gd_2CoSi_2	1.0556	0.4165	1.0075	118.97	0.38753		[3]
Gd_2CoSi_2	1.0554(2)	0.41616(7)	1.0076(2)	119.06(1)	0.38684	6.4	[a]
Tb_2CoSi_2	1.0461	0.4145	1.0011	118.98	0.37973		[3]
Tb_2CoSi_2[c,d]	1.04573(9)	0.41450(4)	1.00062(9)	118.996(7)	0.37936	5.7	[a]
Dy_2CoSi_2	1.0397	0.4135	0.9964	118.87	0.37513		[3]
Dy_2CoSi_2	1.03932(8)	0.41324(3)	0.99615(8)	118.861(5)	0.37470	4.3	[a]
Ho_2CoSi_2	1.0339	0.4123	0.9927	118.71	0.37114		[3]
Ho_2CoSi_2[c]	1.03352(6)	0.41271(2)	0.99283(7)	118.713(5)	0.37141	5.9	[a]
Er_2CoSi_2	1.0276	0.4109	0.9874	118.63	0.36594		[3]
Er_2CoSi_2	1.02733(6)	0.41126(2)	0.98768(6)	118.637(4)	0.36625	3.2	[a]

[a] This work.
[b] Atomic position of Tb_2FeSi_2: (Tb (4i) [−0.0008(4), 0, 0.3261(4)], Tb2 (4i) [0.1910(5), 0, 0.1056(5)], Fe (4i) [0.2743(7), 0, 0.6355(8)], Si1 (4i) [0.3472(9), 0, 0.4322(9)], Si2 (4i) [0.4982(9), 0, 0.1277(8)].
[c] Crystallographic data used with permission of JCPDS – International Centre for Diffraction Data.
[d] Atomic position of Tb_2CoSi_2: (Tb (4i) [−0.0005(3), 0, 0.3240(4)], Tb2 (4i) [0.1827(5), 0, 0.0956(4)], Co (4i) [0.2675(6), 0, 0.6365(8)], Si1 (4i) [0.3462(9), 0, 0.4152(9)], Si2 (4i) [0.4854(9), 0, 0.1258(9)].

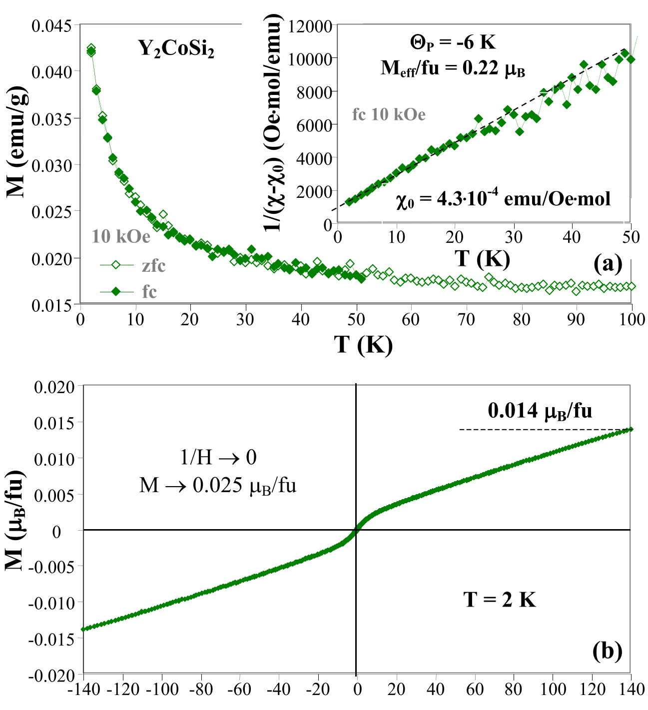

Fig. 1. (a) Magnetization vs. temperature in applied field of 10 kOe and (b) magnetization vs. magnetic field at 2 K of Y_2CoSi_2.

microprobe analysis. The X-ray data were obtained on a Rigaku D/MAX-2500 diffractometer (Cu Kα1 radiation, 2θ=5–120 °, 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 analyses of the samples. Signals averaged over three points per phase were used to estimate standard deviations of 1 at% for rare earth elements (measured by L-series lines), 1 at% for Co and 1 at% for Si (measured by K-series lines). The unit cell data were derived from powder XRD using the Rietan-program [18,19] in the isotropic approximation at room temperature.

DC 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 2–400 K and in magnetic fields up to 140 kOe. Low field (100 Oe) magnetization data were obtained in zero-field-cooled (zfc) and field-cooled (fc) states to determine the magnetic ordering temperatures. The Curie and Néel temperatures (T_C and T_N) were taken corresponding to the extremum point in the dM/dT vs. T plot and maximum in the M vs. T curve, respectively. Magnetization as a function of temperature was measured in field of 5 kOe in zero-field-cooled state to obtain effective paramagnetic moments and paramagnetic Curie temperatures. Magnetization vs. field hysteresis curve was recorded at 2 K and 5 K to obtain saturation magnetic moments, residual magnetization, coercive and critical fields. Magnetization isotherms were obtained at various temperatures, with a temperature step of 5 or 10 K and a field step of 2.5 kOe, to calculate isothermal magnetic entropy changes. The paramagnetic susceptibility was fitted to the Curie–Weiss law and the effective magnetic moments and paramagnetic Curie temperatures were obtained [20]. 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 [21].

3. Results

3.1. Crystal structure

The electron microprobe and X-ray powder diffraction analyses indicate that the 'R_2{Fe, Co}Si_2' samples contain the Sc_2CoSi_2-type R_2{Fe, Co}Si_2 ($R_{40(1)}${Fe, Co}$_{20(1)}Si_{40(1)}$) main phase and 3–8 wt% of admixture CrB- or FeB-type RSi ($R_{50(1)}Si_{(50(1))}$) and $CeGa_2Al_2$-type R{Fe, Co}$_2Si_2$ ($R_{20(1)}${Fe, Co}$_{40(1)}Si_{(40(2))}$) phases (see Tables 1, 1s and microstructure of 'Ho_2CoSi_2' sample as a representative example in Fig. 1s). The admixture $CeGa_2Al_2$-type R{Fe, Co}$_2Si_2$ phases are antiferromagnets with Néel points of 8 K ($GdFe_2Si_2$), 4.2 K ($TbFe_2Si_2$), 43 K ($GdCo_2Si_2$), 45 K ($TbCo_2Si_2$), 20 K ($DyCo_2Si_2$), 11.2 K ($HoCo_2Si_2$) and 6 K ($ErCo_2Si_2$), whereas YCo_2Si_2 is Pauli paramagnet [17]. The admixture RSi phases show antiferromagnetic