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Magnetic order of $Tb_3Co_{2.2}Si_{1.8}$ and $Dy_3Co_{2.2}Si_{1.8}$ as a representative of the family of compounds with orthorhombic distortion of rare earth lattice

A.V. Morozkin [a,*], O. Isnard [b,c], R. Nirmala [d], S.K. Malik [e]

[a] Department of Chemistry, Moscow State University, Leninskie Gory, House 1, Building 3, GSP-2, Moscow 119992, Russia
[b] CNRS, Institut Néel, 25 rue des Martyrs BP166 x, F-38042 Grenoble, France
[c] Université Grenoble Alpes, Institut Néel, F-38042 Grenoble, France
[d] Indian Institute of Technology Madras, Chennai 600036, India
[e] Departamento de Física Teórica e Experimental, Universidade Federal do Rio Grande do Norte, Natal 59082-970, Brazil

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ABSTRACT

Magnetic measurements indicate that the rare earth intermetallic compounds $Tb_3Co_{2.2}Si_{1.8}$ and $Dy_3Co_{2.2}Si_{1.8}$ ($Dy_3Co_{2.2}Si_{1.8}$-type) exhibit ferromagnetic transition at 132 K and 74 K and a spin-reorientation transition around 42 K and 35 K, respectively. Below Curie temperature, both compounds are soft ferromagnets, whereas below the spin reorientation transition they are permanent magnets with antiferromagnetic component: the values of critical field $H_c=30$ kOe, coercive field $H_{coer}=17$ kOe and residual magnetization $M_{res}=4.1$ μ_B/Tb for $Tb_3Co_{2.2}Si_{1.8}$ and $H_c=14$ kOe, $H_{coer}=21.5$ kOe and $M_{res}=3.7$ μ_B/Dy for $Dy_3Co_{2.2}Si_{1.8}$ at 2 K. The magnetocaloric effect of $Dy_3Co_{2.2}Si_{1.8}$ is calculated in terms of isothermal magnetic entropy change (ΔS_m) and it reaches a values of -16.5 J/kg K at 75 K for a field change of 140 kOe (-8.1 J/kg K at 70 K, for 0–50 kOe change) and -6.0 J/kg K for a field change of 140 kOe (-1.4 J/kg K, for 0–50 kOe change) around 40 K.

Neutron diffraction study in zero applied field shows mixed ferro-antiferromagnetic ordering of $Tb_3Co_{2.2}Si_{1.8}$ below ~127 K with wave vectors $\mathbf{K}_0=[0, 0, 0]$ and $\mathbf{K}_1=[\pm K_x, 0, 0]$ ($K_x \approx 3/10$). Between ~127 K and 53 K the magnetic structure of $Tb_3Co_{2.2}Si_{1.8}$ is set of canted ferromagnetic cones with a resulting *b*-axis ferromagnetic component, whereas below 43 K its magnetic structure is set of canted ferromagnetic cones with a resulting *c*-axis ferromagnetic component. Between 53 K and 43 K the high-temperature magnetic order of $Tb_3Co_{2.2}Si_{1.8}$ transforms to the low-temperature order via an intermediate state. The level of orthorhombic distortion of the Tb-sublattice determines the magnetic ordering of $Tb_3Co_{2.2}Si_{1.8}$ in the Tb → $Tb_3Co_{2.2}Si_{1.8}$ → $Tb_3Co_2Ge_3$ → TbGe sequence.

1. Introduction

The rare earth intermetallic compounds $Tb_3Co_{2.2}Si_{1.8}$ and $Dy_3Co_{2.2}Si_{1.8}$ crystallize in the $Dy_3Co_{2.2}Si_{1.8}$-type structure (or W_3CoB_3-type structure, the ordered variant of Er_3Ge_4-type structure), like the Er_3FeGe_3 [1], $Gd_3Co_{2.48}Si_{1.52}$ [2], {Y, Gd, Dy–Tm}$_3Co_{2.2}Si_{1.8}$ [3] and {Y, Pr, Nd, Sm, Gd, Tb}$_3Co_3Ga$ [4]. These compounds belong to a large family of the two-layer orthorhombic structures with the *Cmcm* space group symmetry as shown in [3] that can be derived from the Mg-type rare earth via orthorhombic distortion of the initial hexagonal rare-earth lattice with the insertion of transition metals and *p* elements. Due to structural changes, incorporation of transition metals and *p* elements modifies the magnetic interactions between the rare-earth atoms. The magnetic structure of *Cmcm* two-layer Tb-containing compounds was investigated for the CrB-type $TbSi_{1-x}Ge_x$ [5,6], $CeNiSi_2$-type $TbCo_{0.5}Ge_2$ [7], $YNiAl_4$-type $TbNiAl_4$ [8] and $Hf_3Ni_2Si_3$-type $Tb_3Co_2Ge_3$ [9] compounds. From preliminary investigation of magnetic properties, $Tb_3Co_{2.2}Si_{1.8}$ and $Dy_3Co_{2.2}Si_{1.8}$ compounds were found to exhibit mixed ferro-antiferromagnetic ordering below 127 and 73 K, respectively [1].

The investigation of magnetic ordering of the $Tb_3Co_{2.2}Si_{1.8}$ and $Dy_3Co_{2.2}Si_{1.8}$ in detail supplements the series of *Cmcm* two-layer rare earth compounds and permits to understand the magnetic ordering of compounds with orthorhombic distortion of initial

* Corresponding author.
E-mail address: morozkin@tech.chem.msu.ru (A.V. Morozkin).

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Table 1a
Unit cell data of $Dy_3Co_{2.2}Si_{1.8}$-type $Tb_3Co_{2.2}Si_{1.8}$ and $Dy_3Co_{2.2}Si_{1.8}$ (space group *Cmcm*, *N* 63, *oC*28, *Z*=4) [a] [1].

Compound	*a* (nm)	*b* (nm)	*c* (nm)	*a*/*b*	*a*/*c*	*b*/*c*	*V* (nm^3)	R_F (%)
$Tb_3Co_{2.2}Si_{1.8}$ [b]	0.40967(2)	1.02439(3)	1.27102(3)	0.39992	0.32232	0.80596	0.533399	3.1
$Dy_3Co_{2.2}Si_{1.8}$ [c]	0.40828(1)	1.01898(3)	1.26913(4)	0.40068	0.32170	0.80290	0.527995	3.6

[a] Data used with permission – © JCPDS – International Centre for Diffraction Data.
[b] Tb1 (8f) [0, 0.2782(4), 0.6051(5)], Tb2 (4*c*) [0, 0.0075(4), 1/4], Co (8*f*) [0, 0.4370(6), 0.0900(4)], M1 (4*a*) [0, 0, 0], M2 (4*c*) [0, 0.309(1), 1/4], M1=M2=$Co_{0.1}Si_{0.9}$. β_{11}=0.014896. β_{22}=002382, β_{33}=0.001548 (PDF #00-063-30406).
[c] Dy1 (8f) [0, 0.2775(4), 0.6048(2)], Dy2 (4*c*) [0, 0.0056(2), 1/4], Co (8*f*) [0, 0.4345(6), 0.0881(5)], M1 (4*a*) [0, 0, 0], M2 (4*c*) [0, 0.3038(8), 1/4], M1=M2=$Co_{0.1}Si_{0.9}$. β_{11}=0.014997. β_{22}=002408, β_{33}=0.001552 (PDF #00-0I0-02971, $\beta_{11}=B_{11}/[2a]^2$, $\beta_{22}=B_{22}/[2b]^2$, $\beta_{33}=B_{33}/[2c]^2$).

Table 1b
Interatomic distances of $Tb_3Co_{2.2}Si_{1.8}$: in the table are given the ratio of interatomic distances to the sum of the atomic radii of the corresponding atoms (for M1 and M2 atoms the $r_{M1,M2}=0.1\cdot r_{Co}+0.9\cdot r_{Si}$) [20] $\Delta=D/(r_{atom1}+r_{atom2})$ and coordination numbers δ. The shortest Tb–Tb and Co–Co distances are selected by a bold character. ESD 0.0005 nm.

Atom -Atom	*D* (nm)	Δ	Atom-Atom	*D* (nm)	Δ
Tb1-2M2	0.28958	0.98	Co-1M2	0.24197	0.99
1Co	0.29238	0.97	2M1	0.24333	1.00
1Co	0.29657	0.98	1Co	**0.26268**	1.05
2Co	0.30154	1.00	1Tb1	0.29238	0.97
1M1	0.31474	1.06	1Tb1	0.29657	0.98
2M1	0.33381	1.13	2Tb2	0.29754	0.98
2Tb1	**0.34158**	0.96	2Tb1	0.30154	1.00
1Tb2	**0.34579**	0.97		δ=**10**	
2Tb2	**0.35223**	0.99			
1Tb1	0.36834	1.04	M1 -4Co	0.24333	1.00
	δ=**15**		2Tb1	0.31474	1.06
			2Tb2	0.31785	1.07
Tb2-2M2	0.28863	0.97		δ=**8**	
4Co	0.29754	0.98			
1M2	0.30885	1.04	M2 -2Co	0.24197	0.99
2M1	0.31785	1.07	2Tb2	0.28863	0.97
2Tb1	**0.34579**	0.97	4Tb1	0.28958	0.98
4Tb1	**0.35223**	0.99	1Tb2	0.30885	1.04
	δ=**15**			δ=**9**	

Mg-type rare earth lattice.

2. Experimental details

The $Tb_3Co_{2.2}Si_{1.8}$ and $Dy_3Co_{2.2}Si_{1.8}$ were prepared by arc-melting the weighed amounts of Tb, Dy (99.9 wt%), Co (99.95 wt%) and Si (99.99 wt%). The samples were annealed at 1070 K for 175 h in an argon atmosphere and subsequently quenched in ice-cold water. The quality of the samples was evaluated using powder X-ray diffraction and microprobe analyses. The X-ray data were obtained on a DRON-3.0 and Rigaku d/max-2500 diffractometers (CuKα radiation, 2θ=5–120°, step 0.02°, 4 s per step). An INCA-Energy-350 X-ray EDS spectrometer (Oxford Instruments) on a 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 analysis of the sample. Signals averaged over three points per phase estimated standard deviations of 1 at% for terbium and dysprosium (measured by L-series lines), 1 at% for cobalt and 1.5 at% for silicon (measured by K-series lines).

Magnetization measurements on bulk polycrystalline $Tb_3Co_{2.2}Si_{1.8}$ and $Dy_3Co_{2.2}Si_{1.8}$ 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. The magnetization data (in fields of 100 Oe and 5 kOe) were obtained in zero-field-cooled (zfc) and field-cooled (fc) states to determine the magnetic ordering temperatures, effective paramagnetic moments and paramagnetic Curie temperatures. Magnetization vs. field hysteresis curve was recorded to obtain saturation magnetic moments and coercive fields. Magnetization isotherms of $Dy_3Co_{2.2}Si_{1.8}$ were obtained at various temperatures ranging from 30 K to 125 K with a temperature step of 5 K and a field step of 2.5 kOe to calculate isothermal magnetic entropy changes.

Neutron diffraction experiments were carried out at the high flux reactor of the Institut Laue Langevin (Grenoble, France) using the high flux powder diffractometer D1B [10] from 150 down to

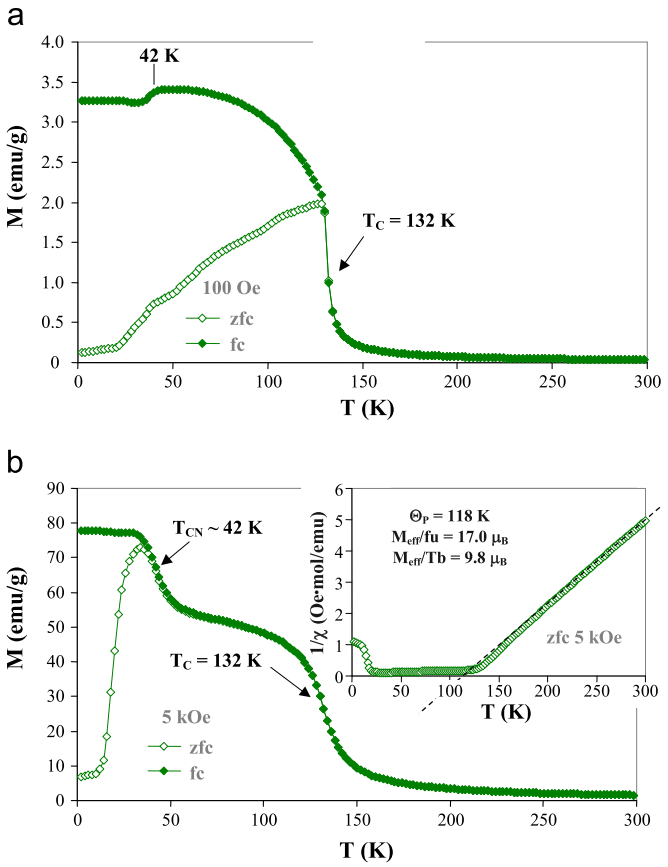

Fig. 1. Magnetization of $Tb_3Co_{2.2}Si_{1.8}$ as a function of temperature in an applied fields of (a) 100 Oe and (b) 5 kOe Oe (inset in (a, b): inverse magnetic susceptibility vs. temperature and the Curie–Weiss fit).