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Crystal structure and magnetic properties of the $RCo_{5-x}Ga_x$ ($x=1$, 1.5, 2, 3, 4) and $RCo_{4-x}FeGa_x$ ($x=1$, 2) compounds (R=rare earth)

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Abstract

X-ray powder diffraction data of the $RCo_{5-x}Ga_x$ compounds indicate that single-phase samples of the $CaCu_5$ type structure exist up to the composition RCo_3Ga_2. The compounds with light rare earths are ferromagnets while those with heavy rare earths are ferrimagnets. The introduction of Fe into the $RCo_{5-x}Ga_x$ compounds has an important effect on the magnetic properties. © 1998 Elsevier Science S.A.

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1. Introduction

RCo_5 compounds, with the hexagonal structure of $CaCu_5$-type, play an important role in the research of rare earth–3d metal compounds, from both technological and fundamental points of view. Well-known examples are permanent magnet materials based on the RCo_5 family. As an extension of the research on RCo_5, substituted $RCo_{5-x}Ga_x$ ($x=1$, 2, 4) systems have been published recently [1–4].

We have also reported on the magnetic properties of the $RCo_{4-x}FeGa_x$ ($x=1$, 2) compounds [5,6] because the introduction of iron atoms into the $RCo_{5-x}Ga_x$ compounds influences the magnetic properties markedly.

2. Crystal structure

$RCo_{5-x}Ga_x$ compounds were prepared as described in Ref. [1]. For R=Ce, Pr, Nd, Gd, Tb, Dy, Ho, Er with $x=1$, 1.5, 2, 3, and 4 analysis showed that single-phase compounds, crystallizing in the hexagonal $CaCu_5$-type crystal structure, form in this system only for $x\leq 2$. A similar type of patterns were also observed in the X-ray diagrams of the samples with $x=3.0$, although many other lines were present indicating that the samples probably are not single phase.

Finally, $RCoGa_4$ compounds (R=Ce, Pr, Nd) crystallize in the orthorhombic Cmcm space group [7]. The $RCoGa_4$ compounds with heavy rare earths do not form.

In RCo_5 compounds, with the hexagonal $CaCu_5$-type structure there is one site for rare earth metals 1a(0,0,0) and two different cobalt sites,

$2c(\frac{1}{3},\frac{2}{3},0)$

and

$3g(\frac{1}{2},0,\frac{1}{2})$.

In RCo_4Ga and RCo_3Ga_2 compounds, there is one rare earth site, (a:0,0,0), but the Ga atoms prefer the 3g site in agreement with previous neutron diffraction investigations in $RCo_{5-x}Ga_x$ compounds [8–10]. The unit cell parameters and the atom positions of $TbCo_{5-x}Ga_x$ compounds are presented in Table 1 (Lazy-Pulverix program [11]).

The crystal structure for these compounds can also be described by a larger hexagonal unit cell derived from the $CaCu_5$-type stucture when the parameter *a* is increased by

Table 1
$CaCu_5$ type structure

	Atom	Position	*x*	*y*	*z*	Occup.
$TbCo_4Ga$	Tb	1a	0.0	0.0	0.0	1
$a=5.018$	Co	2c	$\frac{1}{3}$	$\frac{2}{3}$	0	1
$c=4.022$	Co	3g	$\frac{1}{2}$	0	$\frac{1}{2}$	0.67
	Ga	3g	$\frac{1}{2}$	0	$\frac{1}{2}$	0.33
$TbCo_{3.5}Ga_{1.5}$		$a=5.025$		$c=4.063$		
$TbCo_3Ga_2$	Tb	1a	0.0	0.0	0.0	1
$a=5.095$	Co	2c	$\frac{1}{3}$	$\frac{2}{3}$	0	1
$c=4.085$	Co	3g	$\frac{1}{2}$	0	$\frac{1}{2}$	0.33
	Ga	3g	$\frac{1}{2}$	0	$\frac{1}{2}$	0.67

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Table 2
Larger cell

	Atom	Position	*x*	*y*	*z*	Occup.
$TbCo_4Ga$	Tb_I	1a	0.0	0.0	0.0	1
$a = 8.688$	Tb_{II}	2c	$\frac{1}{3}$	$\frac{2}{3}$	0.0	1
$c = 4.025$	Co_I	6j	$\frac{1}{3}$	0.0	0.0	1
	Co_{II}	6m	$\frac{1}{6}$	$\frac{1}{3}$	$\frac{1}{2}$	1
	Ga	3g	$\frac{1}{2}$	0.0	$\frac{1}{2}$	1
$TbCo_{3.5}Ga_{1.2}$		$a = 8.701$		$c = 4.069$		
$TbCo_3Ga_2$	Tb_I	1a	0.0	0.0	0.0	1
$a = 8.827$	Tb_{II}	2c	$\frac{1}{3}$	$\frac{2}{3}$	0.0	1
$c = 4.044$	Co_I	6j	$\frac{1}{3}$	0.0	0.0	1
	Co_{II}	6m	$\frac{1}{6}$	$\frac{1}{3}$	$\frac{1}{2}$	0.5
	Ga	6m	$\frac{1}{6}$	$\frac{1}{3}$	0.5	
	Ga_{II}	3g	$\frac{1}{2}$	0.0	$\frac{1}{2}$	1

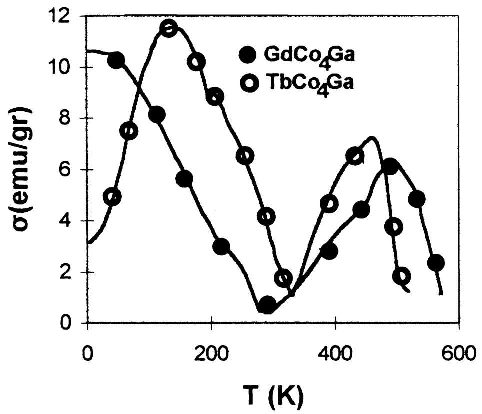

Fig. 1. Temperature dependence of magnetization up to 600 K for $GdCo_4Ga$ and $TbCo_4Ga$ compounds.

a factor of $\sqrt{3}$ [12,13]. In this case of a larger cell, comparison between observed and calculated intensity values showed the best agreement with the atomic positions presented in Table 2.

Neutron diffraction measurements on the $TbCo_3Ga_2$ compound [14] confirmed the atom position given in Table 2 but not the RCo_3Ga_2 atom position proposed by Fremy et al. [12]: R_I at 1b (0°,0°,0.5) R_{II} at 2C($\frac{1}{2}$,$\frac{2}{3}$,0), Co_I at 3g(0.5,0.0,0.5) Co_{II} at 6m(0.1799,0.3598,0.5) and Ga at 6j(0.2895,0.0,0).

The lattice parameters of $RCo_{4-x}FeGa_x$ ($x = 1$, 2) increase in relation to those of the $RCo_{5-x}Ga_x$ compounds. This is due to the fact that the ionic radius of Fe is greater than that of Co.

3. Magnetic measurements

The magnetic measurements of the $RCo_{5-x}Ga_x$ compounds were performed by a vibrating sample magnetometer for fields up to 20 kOe, while those of $RCo_{4-x}FeGa_x$ with a SQUID magnetometer in the temperature range 4.2–300 K and with a vibrating sample magnetometer in the temperature range 300–1200 K for magnetic fields of 1–20 kOe.

RCo_4Ga compounds show ferromagnetic behaviour for light rare earths, while the compounds with heavy rare earths are ferrimagnets (Fig. 1).

RCo_3Ga_2 compounds show ferromagnetic behaviour, while neutron diffraction on powdered samples of

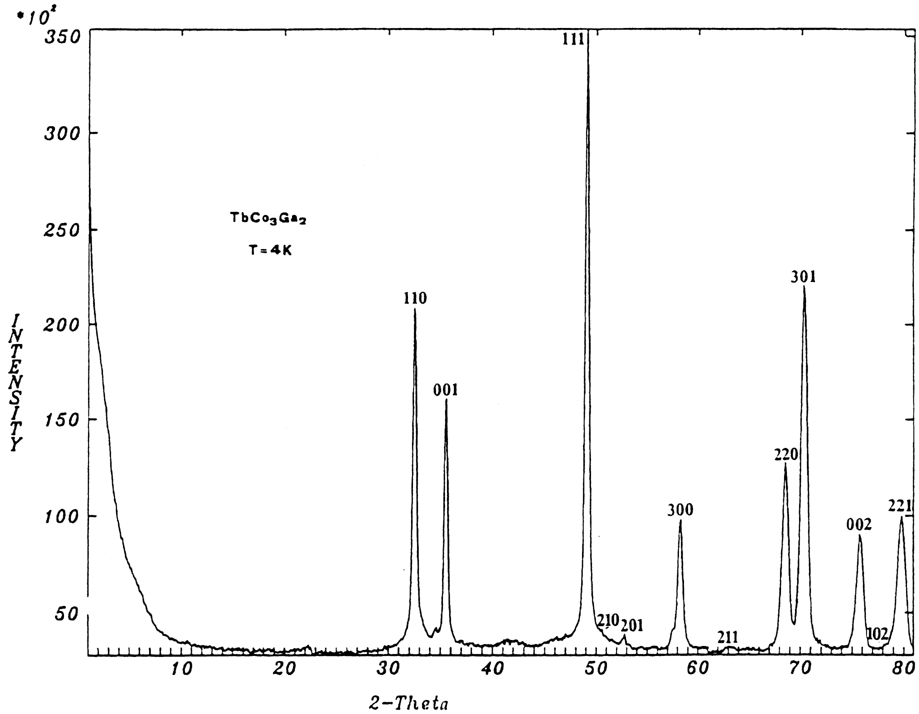

Fig. 2. Neutron diffraction diagram fo $TbCo_3Ga_2$ at 4 K.

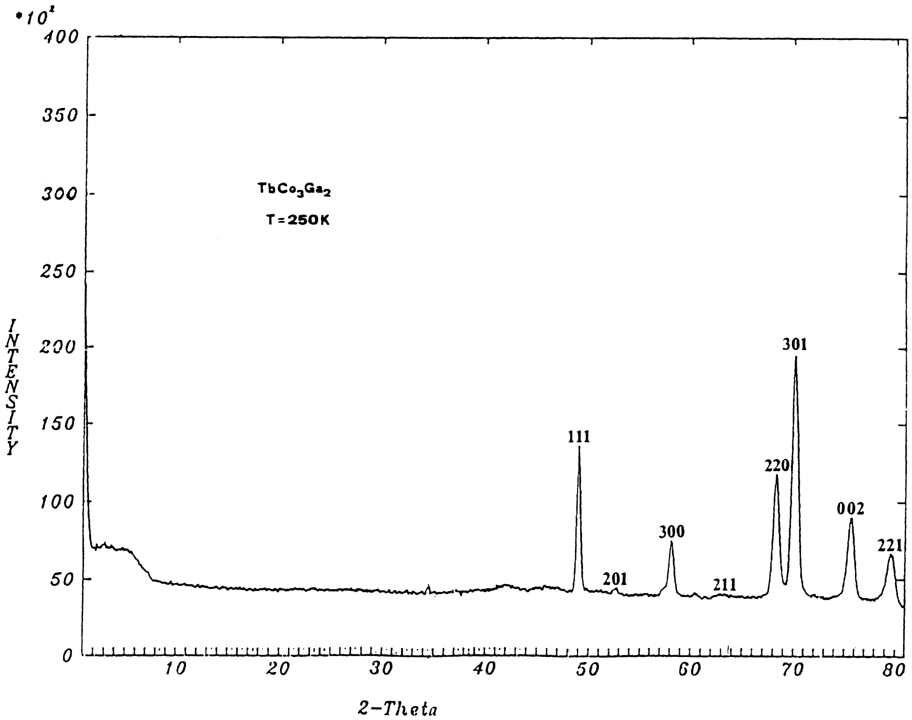

Fig. 3. Neutron diffraction diagram of $TbCo_3Ga_2$ at 250 K.

$TbCo_3Ga_2$ showed that the magnetic structure at 4 K is collinear ferrimagnetic with the magnetic moment of terbium (7 μ_B) and cobalt (-0.4 μ_B) sublattice in opposite directions perpendicular to the c-axis [14] Fig. 2 Fig. 3.

This result is in agreement with the fact that the $TbCo_5$ and $TbCo_4Ga$ compounds have, as the easy plane of magnetization at low temperature, the plane normal to the c-axis [15,16], in accordance with a recent publication that the easy magnetization direction of $GdCo_3Ga_2$ is perpendicular to the c-axis [17].

The $RCoGa_4$ compounds (R = Ce, Pr, Nd) present paramagnetic behaviour down to 4.6 K [4].

Gallium substitution leads to a large decrease of cobalt magnetic moment and T_{ord} in RCo_5. Hysteresis is observed for $M(T)$ measurements in $RCo_{5-x}Ga_x$ compounds. This hysteresis can be attributed to the domain wall pinning.

The introduction of iron into the $RCo_{5-x}Ga_x$ compounds increases the Curie temperature and causes the compensation point to shift towards lower temperatures (for example, $TbCo_4Ga$ has $T_{comp} = 320$ K while $TbCo_3FeGa$ has $T_{comp} = 290$ K).

The increase of iron content in the $RCo_{4-x}FeGa_x$ ($x = 1$, 2) compounds enhances the magnetic 3d sublattice moment and decreases the axial 3d sublattice magnetocrystalline anisotropy.

References

[1] Ch.D. Routsi, J.K. Yakinthos, E. Gamari-Seale, J. Magn. Magn. Mater. 102 (1991) 275.

[2] Ch.D. Routsi, J.K. Yakinthos, E. Gamari-Seale, J. Magn. Magn. Mater. 102 (1991) 266.

[3] Ch.D. Routsi, J.K. Yakinthos, E. Gamari-Seale, J. Magn. Magn. Mater. 116 (1992) 99.

[4] Ch.D. Routsi, J.K. Yakinthos, E. Gamari-Seale, J. Magn. Magn. Mater. 116 (1992) 397.

[5] Ch.D. Routsi, J.K. Yakinthos, S. Hatzivasiliou, J.K. Yakinthos, J. Tsoukalas, J. Alloys Compounds 10 (1994) 305.

[6] Ch.D. Routsi, J.K. Yakinthos, H. Gamari-Seale, J. Magn. Magn. Mater. 137 (1994) 98.

[7] O.M. Sinevich, Metallofiz. Ukrainian SSR 10 (1988) 116.

[8] P. Schobinger-Papamantellos, D.P. Middleton, K.H.J. Bushow, J. Alloys Compounds 206 (1994) 189.

[9] O. Moze, K.H.J. Buschow, Journal of Magnetism and Magnetic Materials 146 (1995) 111–116.

[10] C.V. Thang, P.E. Brommer, J.H.P. Copla, E. Bruck, A.A. Menovsky, N.P. Thuy, J.J.M. Franse, J. Alloys Compounds 245 (1996) 100.

[11] K. Yvon, W. Jeitschko, Parthe, J. Appl. Crystallogr. 10 (1977) 73.

[12] M.A. Fremy, D. Gignoux, J.M. Moreau, D. Paccard, L. Paccard, J. Less-Common Metals 106 (1985) 251.

[13] I. Felner, A. Grayevsky, N. Kaplan, J. Magn. Magn. Mater. 81 (1989) 179.

[14] Ch.D. Routsi, J.K. Yakinthos, E. Ressouche, J. Alloys Compounds 256 (1997) 61.

[15] R. Lemaire, Cobalt 32 (1966) 132.

[16] H. Ido, K. Konno, T. Ito, S.F. Cheng, S.G. Sankar, W.E. Wallace, J. Magn. Magn. Mater. 104–107 (1992) 1361–1362.

[17] F.M. Mulder, R.C. Thiel, J. Alloys Compounds 210 (1994) 255–255.