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Structure and magnetic properties of $ScFe_6Ga_6$-type RCo_5Ga_7 (R = Y, Tb, Dy, Ho and Er)

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Abstract

The structure and magnetic properties of the RCo_5Ga_7 (R = Y, Tb, Dy, Ho and Er) compounds with the $ScFe_6Ga_6$-type structure have been studied. The stability of RCo_5Ga_7 is closely related with the ratio of the metal radii $R_{RE}/R_{(Co,Ga)}$. With $R_{RE}/R_{(Co,Ga)} \leqslant 1.36$, the compounds can be stabilized in the $ScFe_6Ga_6$-type structure. The lattice of RCo_5Ga_7 shrinks as the atomic order of R increases, and it is consistent with the lanthanide contraction. The structure analysis based on X-ray diffraction patterns reveals that in the orthorhombic RCo_5Ga_7 (*Immm*), R occupies the 2*a* site, and Co enters into the 8*k* and the 4*h* sites, and Ga is at the 4*e*, 4*f*, 4*g*, 4*h* and 8*k* sites. The interatomic distances and the coordination numbers of RCo_5Ga_7 are provided from the refinement results. The short interatomic distance (less than 2.480 Å) between the Co ions results in the negative magnetic interaction, which does not favor ferromagnetic ordering. The magnetic moment of YCo_5Ga_7 is absent, and RCo_5Ga_7 (R = Tb, Dy, Ho and Er) may have long-range magnetic ordering with the paramagnetic Curie temperature lower than 5 K.

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Keywords: Crystal structure; $ScFe_6Ga_6$-type structure; Magnetic ordering

1. Introduction

The compounds of the type RT_6M_6 (R = rare earth, T = transition metal, and M = Ge, Sn and Ga) are very interesting. They can crystallize in a variety of structures depending on the different R and the different preparation techniques [1–5]. Venturini et al. [3] reported that the RMn_6Ge_6 (R = Sc, Y, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu) compounds crystallize in $HfFe_6Ge_6$-type structure, and RMn_6Ge_6 (R = Nd and Sm) crystallize in YCo_6Ge_6-type structure. The different R makes RFe_6Ge_6 (R = Sc, Y, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu) crystallize in different types of structures, including $HfFe_6Ge_6$-type, YCo_6Ge_6-type, $TbFe_6Sn_6$-type, $HoFe_6Sn_6$-type or $GdFe_6Ge_6$-type structure [3]. As for RFe_6Sn_6, a series of superstructures, which consist of different intergrowths of $HfFe_6Ge_6$ and $ScFe_6Ga_6$ slabs, are formed [6]. The physical properties, especially the magnetic properties, of RT_6M_6 (R = rare earth, T = Mn, Fe, Co, and M = Ge, Sn, Ga) are sensitively dependent on the different R, T and M and the annealing conditions [2–3,5,7–11]. Zaharko et al. [9] studied the influence of thermal history on the crystal structure, microstructure and magnetic properties of $TbFe_6Ge_6$. The crystal and magnetic properties of $TbFe_6Ge_6$ strongly depend on the thermal

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history. Moreover, Fedyna et al. [12] and Skolozdra et al. [13] reported that RCo$_6$Ge$_6$ (R = Dy, Er, Tm, and Yb) and RCo$_6$Sn$_6$ (R = Tb, Dy, Ho, Er, and Tm) are paramagnetic in the temperature range 78–293 K. Zhang et al. [14,15] and Venturini et al. [5,16–19] reported that the substitution of Ga for the non-magnetic M could make the antiferromagnetic RMn$_6$M$_6$ become ferrimagnetic RMn$_6$M$_{6-x}$Ga$_x$ with spontaneous magnetization. Weitzer et al. [20] first reported that RFe$_6$Ga$_6$ can crystallize in the ThMn$_{12}$-type structure ($I4/mmm$) or the ScFe$_6$Ga$_6$-type structure ($Immm$) depending on the R size and the annealing temperature. Guo et al. [21] prepared RFe$_6$Ga$_6$ (R = Ce, Pr, Nd, Sm and Gd) with the ScFe$_6$Ga$_6$-type structure, and RFe$_6$Ga$_6$ are ferromagnetic. Thus, our intensive interest in RT$_6$Ga$_6$ is provoked. To our knowledge, no work on the structure and magnetic properties of RCo$_6$Ga$_6$ is reported. In this paper, we will study the structure and magnetic properties of RCo$_5$Ga$_7$ (R = Y, Tb, Dy, Ho and Er) with the ScFe$_6$Ga$_6$-type structure. In the experiments, the attempts to synthesize RCo$_6$Ga$_6$ failed.

2. Experimental

RCo$_5$Ga$_7$ (R = Y, Tb, Dy, Ho and Er) were prepared by arc-melting the constituent elements with appropriate ratio in a high-purified Ar atmosphere. All initial materials were better than 99.9% pure. An excess of R was added to compensate for any subsequent mass loss. The samples were remelted several times to ensure homogeneity. The ingots were then wrapped in Mo foil, sealed in evacuated quartz tubes and annealed at 800 °C for 7 days, and finally quenched by submersing the silica tubes in cold water. The X-ray diffractions were performed on a Rigaku D/max 2500 diffractometer with a rotating target X-ray tube. Cu$K\alpha$ radiation with 40 kV × 250 mA and graphite monochrometer were used at room temperature. For all the samples, the XRD data of RCo$_5$Ga$_7$ were collected with step-scanning mode for structure determination, and the scan range 2θ was from 20° to 120°, with a scanning step of $2\theta = 0.02°$ and a sampling time 2 s. The crystal structure of RCo$_5$Ga$_7$ was refined by using the program DBWS-9411 based on the Rietveld method. The 2θ-zero point was corrected in the calculation of the lattice parameters with standard sample Si, and the average isotropic Debye–Waller factor (B_{iso}) was refined. The magnetization measurements on free powder samples were carried out using a superconducting quantum interference device (SQUID) with a maximum field of 50 kOe.

3. Results and discussion

The XRD diffraction patterns of RCo$_5$Ga$_7$ with R = Y and heavy rare earth R = Tb, Dy, Ho and Er display peaks characterized as the ScFe$_6$Ga$_6$-type structure with CoGa (bcc B2 structure) as impurity. However, with R = light rare-earth element, RCo$_5$Ga$_7$ shows up as a mixture of a few kinds of compounds, and does not form the ScFe$_6$Ga$_6$-type structure. Therefore, the stability of RCo$_5$Ga$_7$ with the ScFe$_6$Ga$_6$-type structure must be closely related with the ratio of the metal radii $R_{RE}/R_{(Co,Ga)}$. With $1.32 \leqslant R_{RE}/R_{(Co,Ga)} \leqslant 1.36$, the RCo$_5Ga_7$ (R = Y, Tb, Dy, Ho and Er) compounds crystallize in the ScFe$_6$Ga$_6$-type structure, and RCo$_5$Ga$_7$ (R = the light rare-earth element) with the ratio $R_{RE}/R_{(Co,Ga)} > 1.36$ fail in forming the ScFe$_6$Ga$_6$-type structure. In the RT$_6$M$_6$-type compounds, although the crystal structures are versatile, they are similar in a sense, and can be treated as the filled derivative structure of binary CoSn-B35. The extremely large R may destroy the stability of the filled structure, and the critical metal radii ratio for RCo$_5$Ga$_7$ is about $R_{RE}/R_{(Co,Ga)} = 1.36$.

The XRD patterns of RCo$_5$Ga$_7$ are refined with the ScFe$_6$Ga$_6$-type structure, as shown in Fig. 1 for YCo$_5$Ga$_7$ by way of example. RCo$_5$Ga$_7$ belongs to the orthorhombic system with space group $Immm$. There are two formulas per unit cell, i.e. each unit cell containing $2R + 10$Co $+ 14$Ga. Table 1 lists the crystallographic parameters including the lattice parameters, the atomic positions, the atomic occupations, the expected factor R_{exp}, the weighted residual factor R_{wp} and the weight percentage of the impurity. With the increasing atomic number of R, the lattice shrinks along all the three directions a, b and c. That is consistent with the lanthanide contraction. The ScFe$_6$Ga$_6$-type structure is a layered structure, as shown in Fig. 2. The orthorhombic ScFe$_6$Ga$_6$-type structure has a close relationship with the tetragonal ThMn$_{12}$-type structure. When the atoms at the 8i and 8j sites in the tetragonal

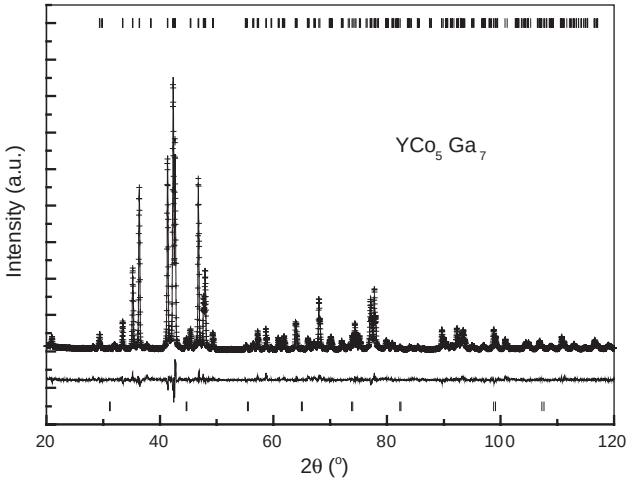

Fig. 1. The refined XRD pattern of YCo$_5$Ga$_7$, the cross symbols and the solid curve are the experimental and the calculated patterns, respectively. The bottom curve is the difference between the experimental and the calculated patterns. The ticks at the top are the peak positions of YCo$_5$Ga$_7$, and the ticks at the bottom are those of CoGa.

Table 1
Refined parameters of $RCo_{5.0+\delta}Ga_{7.0-\delta}$(*Immm*) with 2*a* (0,0,0), 4*e* (*x*,0,0), 4*f* (*x*,1/2,0), 4*g* (0,*y*,0), 4*h* (0,*y*,1/2), and 8*k* (1/4,1/4,1/4), and the weight percentage of the impurity CoGa

$RCo_{5.0+\delta}Ga_{7.0-\delta}$		$YCo_{5.04}Ga_{6.96}$	$TbCo_{5.02}Ga_{6.98}$	$DyCo_{5.01}Ga_{6.99}$	$HoCo_{5.01}Ga_{6.99}$	$ErCo_{5.02}Ga_{6.98}$
a (Å)		8.4845(2)	8.4765(3)	8.4648(2)	8.4600(2)	8.4555(4)
b (Å)		8.4793(1)	8.4772(4)	8.4686(4)	8.4652(3)	8.4577(2)
c (Å)		5.0996(1)	5.0978(2)	5.0899(4)	5.0898(3)	5.0814(4)
V (Å^3)		366.879	366.312	364.870	364.509	363.392
2*R* 2(*a*)	*B* (Å^2)	0.28	0.28	0.28	0.28	0.28
Co 8(*k*)	*B* (Å^2)	0.40	0.40	0.40	0.40	0.40
	Occ.	7.21	7.28	7.16	7.19	7.23
Co 4(*h*)	*y*	0.7698	0.7682	0.7652	0.7693	0.7678
	B (Å^2)	0.40	0.40	0.40	0.40	0.40
	Occ.	2.86	2.75	2.86	2.83	2.81
4Ga 4(*e*)	*x*	0.3419	0.3487	0.3494	0.3439	0.3425
	B (Å^2)	0.55	0.55	0.55	0.55	0.55
4Ga 4(*f*)	*x*	0.2969	0.3034	0.2971	0.2951	0.3069
	B (Å^2)	0.55	0.55	0.55	0.55	0.55
4Ga 4(*g*)	*y*	0.3401	0.3303	0.3391	0.3348	0.3351
	B (Å^2)	0.55	0.55	0.55	0.55	0.55
Ga 4(*h*)	*y*	0.7698	0.7682	0.7652	0.7693	0.7678
	B (Å^2)	0.55	0.55	0.55	0.55	0.55
	Occ.	1.14	1.25	1.14	1.17	1.19
Ga 8(*k*)	*B* (Å^2)	0.55	0.55	0.55	0.55	0.55
	Occ.	0.79	0.72	0.84	0.81	0.77
R_{exp} (%)		4.83	4.95	4.77	4.35	4.93
R_{wp} (%)		12.62	12.77	12.88	12.84	12.68
CoGa (%)		0.86	0.91	0.99	0.73	0.89

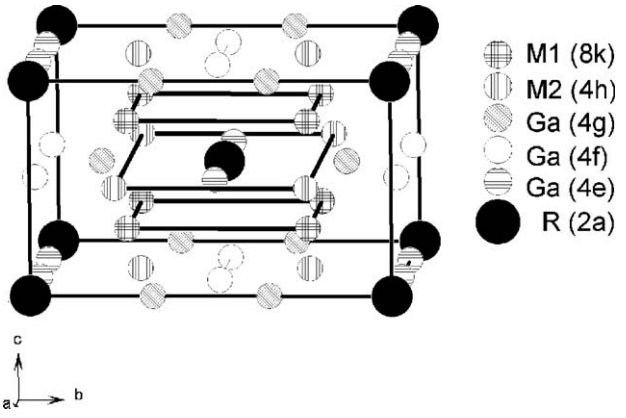

Fig. 2. Layered $ScFe_6Ga_6$-type structure of RCo_5Ga_7 with M_1 (Ga and Co) at the 4*h* site, M_2 (Ga and Co) at the 8*k* site.

$ThMn_{12}$-type structure become ordered, the structure transforms to the orthorhombic $ScFe_6Ga_6$-type with the 8*i* ($ThMn_{12}$)-> the 4*e*, 4*g* ($ScFe_6Ga_6$) and the 8*j* ($ThMn_{12}$)-> the 4*f*, 4*h*($ScFe_6Ga_6$). Even with the small difference between the lattice constants *a* and *b*, as listed in Table 2, the attempts to refine the XRD patterns with the $ThMn_{12}$-type structure failed because of the different atomic occupations between the two structures. In the orthorhombic $ScFe_6Ga_6$-type RCo_5Ga_7, the equivalent 4*e*, 4*g*, and 4*f* sites are only occupied by the Ga atoms due to the atomic ordering. Table 2 lists the interatomic distances and the coordination number of RCo_5Ga_7 calculated based on the XRD refinement results.

The small nearest interatomic distance between the Co ions, less than 2.480 Å, does not favor ferromagnetic coupling due to the negative magnetic interaction, which depends on the distance between the magnetic moment. As shown in Fig. 3, YCo_5Ga_7 has no spontaneous magnetization at 5 K, and the magnetic moment of Co is absent. From the thermal magnetization curves of RCo_5Ga_7 (*R* = Tb, Dy, Ho and Er), as shown in Fig. 4, it cannot be told whether RCo_5Ga_7 (*R* = Tb, Dy, Ho and Er) have long-range magnetic ordering or they are paramagnetic. The inverse magnetizations, i.e. the inverse DC susceptibilities, of RCo_5Ga_7 (*R* = Tb, Dy, Ho and Er) are linear with the temperature higher than 60 K. By fitting the linear part of the $H/M-T$ curves with the Curie–Weiss law $H/M = 1/\chi = (T-\theta)/C$, the paramagnetic Curie temperature of *R*Co5Ga7 (*R* = Tb, Dy, Ho and Er) are obtained as 3.59 K for *R* = Tb, 4.18 K for *R* = Dy, 4.04 K for *R* = Ho, and 3.39 K for *R* = Er. With the low paramagnetic Curie temperatures, RCo_5Ga_7 may have long-range magnetic ordering below 5 K. The low paramagnetic Curie temperature θ agrees with the rather large $R-R$ interatomic distance, $r_{R-R} = c$, which can only contribute weak ferromagnetic coupling. The effective magnetic moments are really near the theoretic rare-earth moments with $\mu_{eff} = 9.56\,\mu_B$ for *R* = Tb, $\mu_{eff} = 10.57\,\mu_B$ for *R* = Dy, $\mu_{eff} = 10.76\,\mu_B$ for

Table 2
Interatomic distance (Å) and coordination number of $RCo_{5+\delta}Ga_{7+\delta}$ with M_1 (Ga and Co) at the 8*k* site and M_2 = (Ga and Co) at the 4*h* site

Atom		Interatomic distance (Å)				
		$YCo_{5.04}Ga_{6.96}$	$TbCo_{5.02}Ga_{6.98}$	$DyCo_{5.01}Ga_{6.99}$	$HoCo_{5.01}Ga_{6.99}$	$ErCo_{5.02}Ga_{6.98}$
M_1 (8*k*)	2 × M_2 (4*h*)	2.480	2.478	2.473	2.474	2.471
	2 × Ga (4*f*)	2.505	2.514	2.502	2.499	2.513
	2 × M_1 (8*k*)	2.550	2.549	2.545	2.545	2.541
	2 × Ga (4*g*)	2.590	2.565	2.582	2.571	2.569
	2 × Ga (4*e*)	2.594	2.611	2.609	2.594	2.588
	2 × Y	3.259	3.257	3.253	3.251	3.249
M_2 (4*h*)	4 × M_1 (8*k*)	2.480	2.478	2.473	2.474	2.471
	2 × Ga (4*f*)	2.604	2.577	2.627	2.611	2.554
	2 × Ga (4*e*)	2.652	2.610	2.582	2.635	2.627
	2 × Ga (4*g*)	2.715	2.682	2.694	2.693	2.686
	2 × Y	3.211	3.218	3.230	3.208	3.211
Ga (4*g*)	4 × M_1 (8*k*)	2.590	2.565	2.582	2.571	2.569
	1 × Ga (4*g*)	2.712	2.877	2.725	2.693	2.686
	2 × M_2 (4*h*)	2.715	2.682	2.694	2.797	2.789
	2 × Ga (4*f*)	2.861	2.947	2.860	2.862	2.946
	1 × Y	2.884	2.800	2.872	2.834	2.834
	2 × Ga (4*e*)	3.184	3.195	3.156	3.190	3.190
Ga (4*f*)	4 × M_1 (8*k*)	2.505	2.514	2.502	2.499	2.513
	2 × M_2 (4*h*)	2.604	2.577	2.627	2.611	2.554
	2 × Ga (4*e*)	2.809	2.856	2.831	2.803	2.837
	2 × Ga (4*g*)	2.861	2.947	2.860	2.862	2.946
	2 × Y	3.077	3.045	3.070	3.079	3.020
Ga (4*e*)	4 × M_1 (8*k*)	2.594	2.611	2.609	2.594	2.588
	1 × Ga (4*e*)	2.652	2.565	2.550	2.635	2.627
	2 × M_2 (4*h*)	2.683	2.610	2.582	2.641	2.663
	2 × Ga (4*f*)	2.809	2.856	2.831	2.803	2.837
	1 × Y	2.901	2.956	2.958	2.909	2.896
	4 × Ga (4*g*)	3.184	3.195	3.156	3.190	3.190
Y	2 × Ga (4*g*)	2.884	2.800	2.872	2.834	2.834
	2 × Ga (4*e*)	2.901	2.956	2.958	2.909	2.896
	4 × Ga (4*f*)	3.007	3.045	3.070	3.079	3.020
	4 × M_2 (4*h*)	3.211	3.218	3.230	3.208	3.211
	8 × M_1 (8*k*)	3.259	3.257	3.253	3.251	3.249

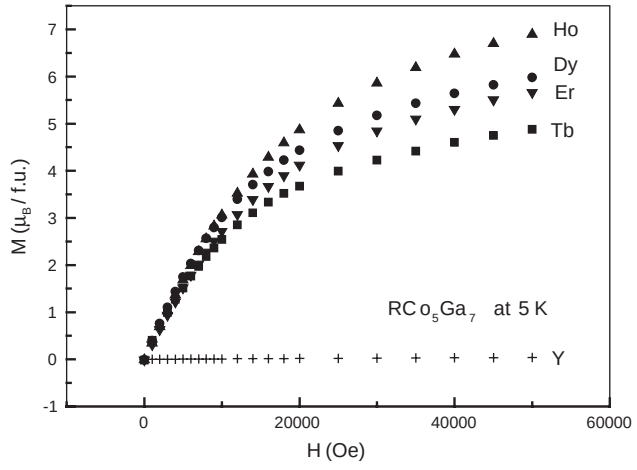

Fig. 3. The magnetization curves of RCo_5Ga_7 (R = Y, Tb, Dy, Ho and Er) at 5 K.

R = Ho and $\mu_{eff} = 10.75\,\mu_B$ for R = Er. The magnetization curves of RCo_5Ga_7 at 5 K are shown in Fig. 3. Depending on the different R, the magnetization of RCo_5Ga_7 (R = Tb, Dy, Ho, and Er) at 5 K ranges from 4.88 μ_B/f.u. to 6.89 μ_B/f.u. in the applied field 50 kOe.

4. Conclusion

RCo_5Ga_7 (R = Y, Tb, Dy, Ho and Er) can form in the $ScFe_6Ga_6$-type structure, and the stability of RCo_5Ga_7 with the $ScFe_6Ga_6$-type structure is closely related with the ratio $R_{Re}/R_{(Co,Ga)}$. With $R_{RE}/R_{(Co,Ga)} > 1.36$, RCo_5Ga_7 (R = light rare-earth) cannot form the $ScFe_6Ga_6$-type structure. RCo_5Ga_7 (R = Tb, Dy, Ho and Er) may have long-range magnetic ordering with the Curie temperature lower than 5 K.

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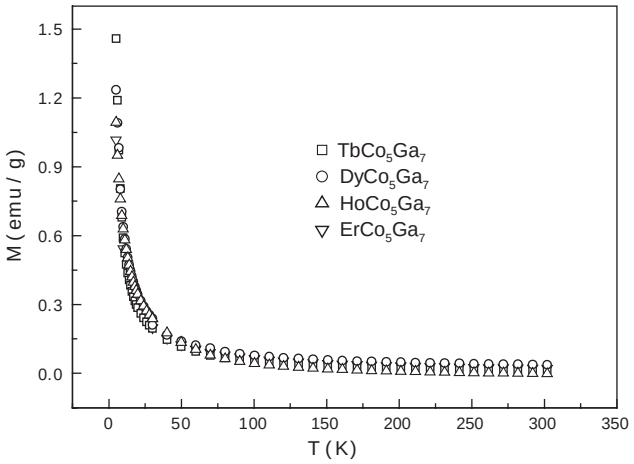

Fig. 4. The thermal magnetization of RCo_5Ga_7 (R = Tb, Dy, Ho and Er) from 5 to 300 K with the applied field 500 Oe.

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