PARAMAGNETIC BEHAVIOUR OF RCo$_4$Si
(R = Gd, Tb, Dy, Ho, Er) INTERMETALLIC COMPOUNDS

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Abstract. The crystal structure and magnetic properties in the paramagnetic range of RCo$_4$Si (R = Gd, Tb, Dy, Ho, Er) intermetallic compounds have been investigated. The compounds crystallise in a hexagonal crystal structure of CaCu$_5$ type, space group P6/mmm. The Curie temperatures range from 336 K (R = Er) to 431 K (R = Gd). The effective cobalt moments were computed assuming an effective rare earth moment as in R^{3+} free ions.

Key words: X-ray diffraction, rare earth-cobalt intermetallic compounds, lattice parameters, Curie temperatures, susceptibility.

INTRODUCTION

The study of magnetic properties of rare earth (R)–3d transition metals (M) intermetallic compounds has been a subject of great interest from both scientific and applications point of view. This interest is explained by the very rich and exceptional properties of these alloys, which arise from the presence in the same compounds of the outer well delocalised 3d electrons and well localised and anisotropic 4f electronic shell. This combination of R and M elements can give rise to materials exhibiting high Curie temperature, given by the strong exchange interaction between 3d electrons of M metals, and a strong anisotropy provided by the rare earth 4f electrons. The most performant permanent magnets of the world, RCo$_5$, R$_2$Co$_{17}$ and R$_2$Fe$_{14}$B type magnets, belong to this class of alloys.

The replacement of Co in the RCo$_5$ compounds by non-magnetic p-elements such as B, Al, Ga or Si results in remarkable effects on the crystallographic and magnetic properties of the host compounds. It is well known that the magnetic properties of cobalt are different on the two inequivalent crystallographic positions

of the CaCu$_5$ structure type. Consequently, the magnetic properties of RCo$_5$ compounds will be influenced by two factors: (a) the substitution of a magnetic element (Co) by a non-magnetic one (B, Ga, Al or Si) and (b) the position where Co is replaced. The preferential occupation of 2c or 3g crystallographic position of Co is given by both the chemical affinity and the size effect. Zlotea and Isnard [1] have shown that the atomic volume allocated for Co in RCo$_5$ structure is greater for Co (3g) than that for Co (2c). The evolution of the metallic radius of Co, B, Ga, Al and Si is known to be 0.92Å (B) < 1.25 Å (Co) < 1.32 Å (Si) < 1.35 Å (Ga) < < 1.43 Å (Al). The replacement of Co by Al, Ga or Si results only in important effects on the magnetic properties, the CaCu$_5$ structure being conserved as in RCo$_5$ compounds. Taking into account both parameters it was shown [1–5] that Al is placed exclusively in Co(3g) site and Ga and Si are distributed over both Co sites with a preference (~ 75÷80%) for 3g site of Co. The smaller radius of B imposes the substitution to take place on the 2c site and leads to a series denoted by R$_{m+n}$Co$_{5m+3n}$B$_{2n}$ with space group symmetry P6/mmm. The crystalline structure consists of systematically stacked m CaCu$_5$-type layers and n CeCo$_3$B$_2$-type layers [6, 7]. If in RCo$_5$ ($m = 1$, $n = 0$) the cobalt magnetisation is well defined and strong [8], in RCo$_3$B$_2$ ($m = 0$, $n = 1$) the intrinsic cobalt magnetisation is nil [9, 10]. This behaviour testifies on the high susceptibility of cobalt magnetisation to magnetic and chemical environment.

For a better understanding of this behaviour, a lot of studies have been done on RCo$_{5-x}$M$_x$ (M = Al, Ga or Si, $x = 0.5$ or 1) compounds [1–5]. The present research work is devoted to complete this systematic study of the RCo$_4$M compounds, the aim is to achieve a better description of the itinerant electron magnetism of the Co sublattice. Herein, we report on the synthesis, crystal structure and magnetic properties of the RCo$_4$Si (R = Gd, Tb, Dy, Ho or Er) compounds.

2. EXPERIMENTAL

Polycrystalline RCo$_4$Si samples (R = Gd, Tb, Dy, Ho, Er) were prepared by the arc melting technique in a cold copper crucible under an argon atmosphere, using elements of purity better than 99.9 percent. A small excess of rare earth was used in the starting material to offset the loss due to evaporation and thus to avoid the formation of Co rich phases with higher Curie temperatures. To ensure a good homogeneity, the compounds were remelted four times, each time the sample was turned. All the samples were remelted in high frequency induction furnace under purified argon atmosphere and then cooled down rapidly to room temperature. The homogeneity of the sample was checked by conventional X-ray powder diffraction,

XRD, with Cu K$_\alpha$ radiation. For these experiments, a *SIEMENS D500* and a *D8 Advance* powder diffractometers were used.

Magnetic measurements were performed using an extraction method [11] in the temperature range 300–900 K and fields of up to 9 T. Magnetic measurements performed in 0.1 T magnetic field in the temperature range 4–800 K allow us to evaluate the transition temperatures. Also, the magnetic ordering temperatures have been determined in low magnetic field with a Faraday type balance at heating and cooling rates of 5 K per minute. A sample of ca. 50 to 100 mg was sealed under vacuum in a small silica tube in order to prevent oxidation of the sample during heating. In order to avoid the alterations of the magnetic susceptibility by the possible presence of small quantities of magnetic phases at temperatures higher than the Curie temperature, the magnetic susceptibilities, χ, were determined from *M/H* field dependencies according with the relation:

$$\frac{M}{H} = \chi + \frac{cM_s}{H} \tag{1}$$

by extrapolation to $H^{-1} \to 0$. The impurity content is represented by *c*, whereas M_s corresponds to the saturation magnetisation of the impurity phase. The magnetic measurements above the Curie temperatures show an independent behaviour of *M/H vs.* magnetic field *H*, showing the absence of any magnetic impurity in all the samples. This fact allows us to perform additional magnetic measurements from 300 to 1000 K in a field of about 0.8 T by using the horizontal translation Weiss magnetic balance.

3. RESULTS AND DISCUSSIONS

The X-ray diffractograms reveal the formation of the RCo$_4$Si (R = Gd, Tb, Dy, Ho, Er) compounds adopting the CaCu$_5$-type structure having the space group *P6/mmm*. The X-ray diffractograms for RCo$_4$Si (R = Gd, Tb, Dy, Ho, Er) compounds are presented in Fig. 1. It is worth noting that unlike the light rare earth RCo$_4$Si containing compounds which were found to be multiphase, the RCo$_4$Si with heavy rare earth are found to be single phase when rapidly quenched in the copper crucible after the melt in induction furnace. The lattice parameters are presented in Table 1. The present lattice parameters are somewhat different from these reported previously by Thang *et al.* [12]. However, it turns out that the lattice parameters given by Thang *et al.* for the RCo$_4$Si compounds correspond to the one of the pure RCo$_5$ determined by Lemaire *et al.* [13]. The values of the *a* parameter do not differ significantly to those of RCo$_5$ compounds. The difference is less than 0.5%. The *c* parameter is little reduced by Si for Co substitution. Indeed the *c*

parameter decreases by about 1.6%, this bears witness to the fact that Si has a smaller size than Co in the RCo_5 compounds. It is worth recalling that the large c parameter observed in pure RCo_5 compounds with heavy rare earth is known to be due to the presence of the Co dumb-bells leading to overstoichiometry of RCo_{5+x} type. It is well known that in the RCo_5 compounds, the c lattice parameter is determined by the cobalt size. As can be seen from Table 1, in the RCo_4Si compounds like in the RCo_5 one, the c lattice parameter is almost constant along the studied series (from R = Gd to Er). On the contrary, the a lattice parameter is
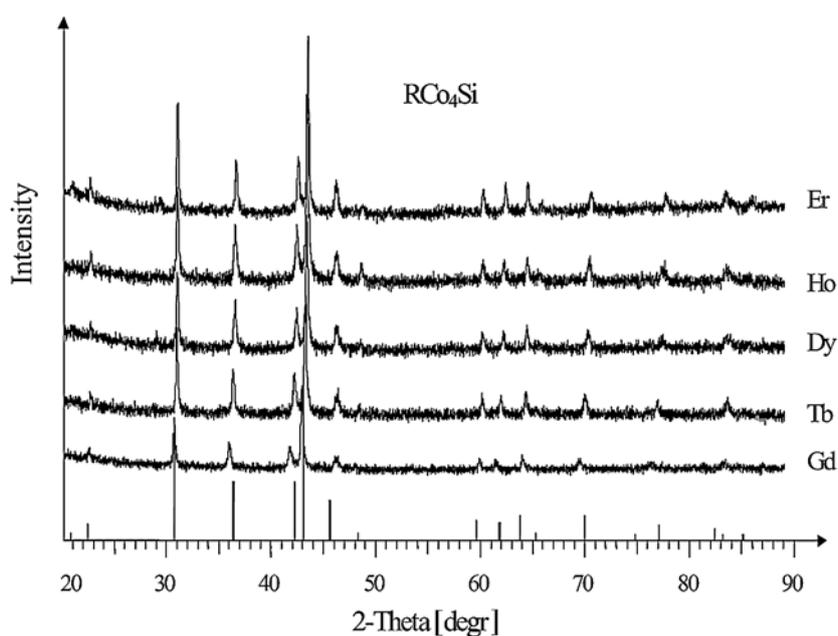

Fig. 1 – The X-ray diffractograms for RCo_4Si (R = Gd, Tb, Dy, Ho, Er) compounds at room temperature. The characteristic diffraction lines for $TbCo_5$ are given.

Table 1

Lattice parameters of the RCo_5 and RCo_4Si intermetallic compounds

R	RCo_4Si		RCo_5 [8, 13]	
	a [nm]	c [nm]	a [nm]	c [nm]
Gd	0.4986(3)	0.3929(3)	0.4976	0.3973
Tb	0.4951(6)	0.3921(6)	0.4946	0.3980
Dy	0.4927(2)	0.3930(2)	0.4933	0.3983
Ho	0.4922(4)	0.3928(4)	0.4911	0.3993
Er	0.4906(4)	0.3930(4)	0.4883	0.4007

much more sensitive to the lanthanide contraction and a significant reduction of a is observed when going from Gd to Er.

Magnetisation measurements in low magnetic field allow us the determination of the Curie temperatures. The Curie temperatures were determined from M^2 *vs.* temperature variation near T_c, Fig. 2 and are summarized in Table2.

The Curie temperatures, T_c, are significantly reduced in comparison with that of the RCo_5 compounds, Table 2. A decrease by 600÷670 K found in RCo_4Si

Table 2

The Curie temperatures of the RCo_4Si intermetallic compounds. For comparison, the Curie temperatures of RCo5 and RCo_4M (M = Ni, Al, Ga) compounds are also given.

R	T_c [K] RCo_4Si	T_c [K] RCo_5 [8, 13]	T_c [K] RCo_4Ni [8]	T_c [K]* RCo_4Al	T_c [K]** RCo_4Ga
Gd	431±7	1008	–	545	500
Tb	385±7	980	785	505	493
Dy	360±7	966	–	479	475
Ho	335±7	1000	852	525	480
Er	336±7	986	–	500	485

* from references [4, 5,17, 18]
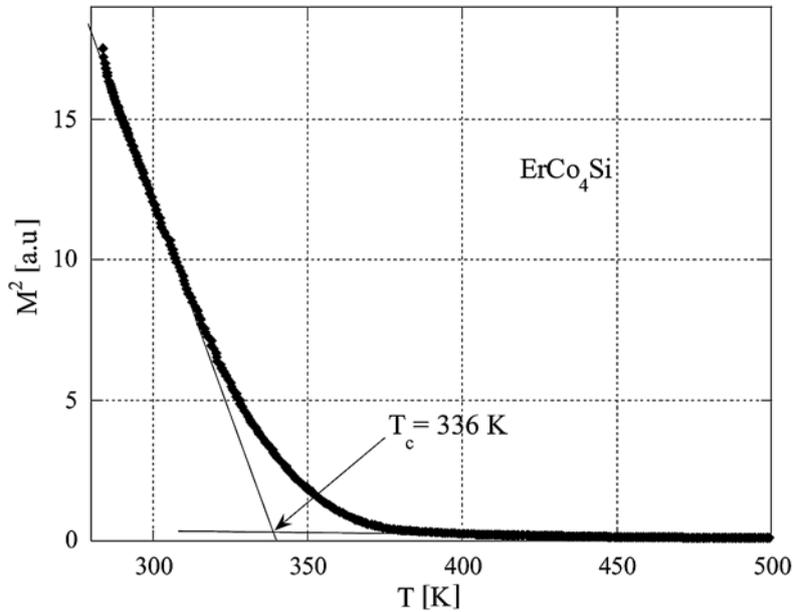** from references [1, 4, 5, 18]

Fig. 2 – Thermo magnetic investigation of the $ErCo_4Si$, showing the Curie temperature at 336 K.

intermetallic compounds is greater than the decrease by about 500 K in RCo_4X (X = Al or Ga) compounds, which is greater than a diminution of only 150÷200 K observed in RCo_4Ni compounds. A common feature in all these compounds is that one Co atom in RCo_5 compounds was replaced by another one, preserving the $CaCu_5$-type crystalline structure. The difference consists in the different electronic structure of the X element. The Ni for Co substitution results in a decrease of T_c as a consequence of replacing a 3*d* magnetic metals, Co, by a 3*d* nonmagnetic metals, Ni (Ni is non magnetic in RNi_5 compounds). The bigger reduction of T_c values when Co is substituted by Al, Ga or Si results from the substitution of a 3*d* magnetic metals, Co, by nonmagnetic *p* elements. The (Co)*d* – *(X)p* hybridisation results in a supplementary reduction of the exchange interactions and consequently of the Curie temperatures. The two electrons in the outer *p* shell of Si are responsible for the bigger decrease of the T_c values in RCo_4Si compounds.

Magnetic measurements have been performed at high temperature for all the studied compounds in order to investigate the magnetic behaviour of the magnetic ions in the paramagnetic range. Above the Curie temperature, the reciprocal susceptibility of RCo_4Si (R = Gd, Tb, Dy, Ho, Er) compounds, Figs. 3 and 4, obeys a Néel-type behaviour, characteristic for ferrimagnetic ordering [14]:

$$\frac{1}{\chi} = \frac{1}{\chi_0} + \frac{T}{C} - \frac{\sigma}{T - \theta} \qquad (2)$$

where $C = \sum C_i$, is the Curie constant of the compounds, C_i are the Curie constants of the magnetic ions involved in each compound, χ_0, σ and θ are connected to the molecular field coefficients and to C_i. In the high temperature range, according to relations (2), the reciprocal magnetic susceptibility behaviour can be approximated by:

$$\frac{1}{\chi} \approx \frac{1}{\chi_0} + \frac{T}{C} \qquad (3)$$

The Curie constants of the RCo_4Si (R = Tb, Dy, Ho, Er) compounds computed in accord with the relations (3) are given in Table 3. The linear fit of the experimental data is given by solid lines in Figs. 3 and 4. The effective cobalt moment, μ_{eff} (Co), was evaluated by assuming an effective rare earth moment as in R^{3+} free ions, assumption which is well satisfied in rare earth–3d transition metals intermetallic compounds [15]. The obtained values are presented in Table 3. In the RCo_4Si the effective cobalt moment is found to be $3.1 \pm 0.1\mu_B$, being almost the same for R = Tb, Dy, Ho, Er. This value is in good agreement with the effective cobalt moments of 3.25 μ_B/Co found by Burzo in $GdCo_4Si$ [16]. The 4 K spontaneous magnetisation of the RCo_4Si (R = Tb, Dy, Ho, Er) compounds are situated between 3.8 and 4.5 μ_B per formul unit, Table 3. Substracting the R^{3+}
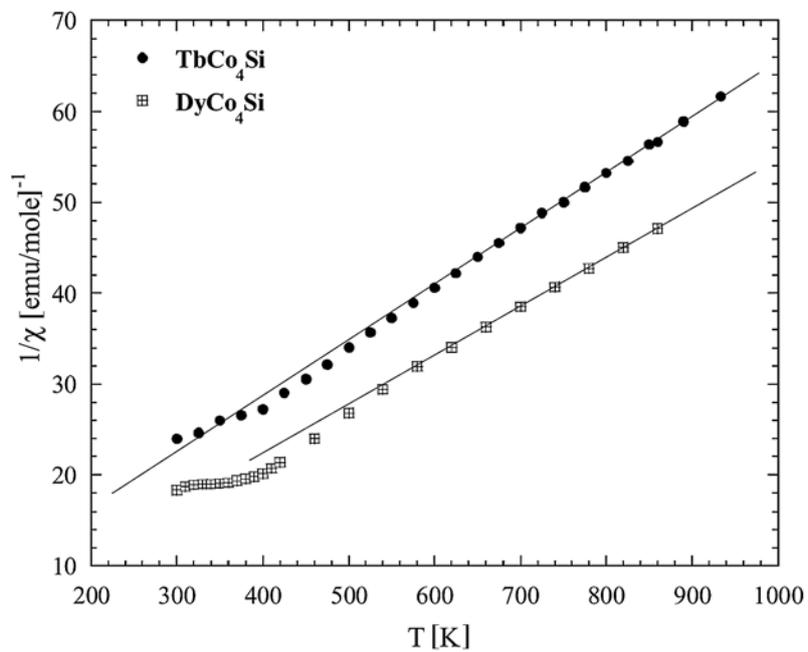
Fig. 3 – The temperature dependence of reciprocal susceptibility for TbCo$_4$Si and DyCo$_4$Si.
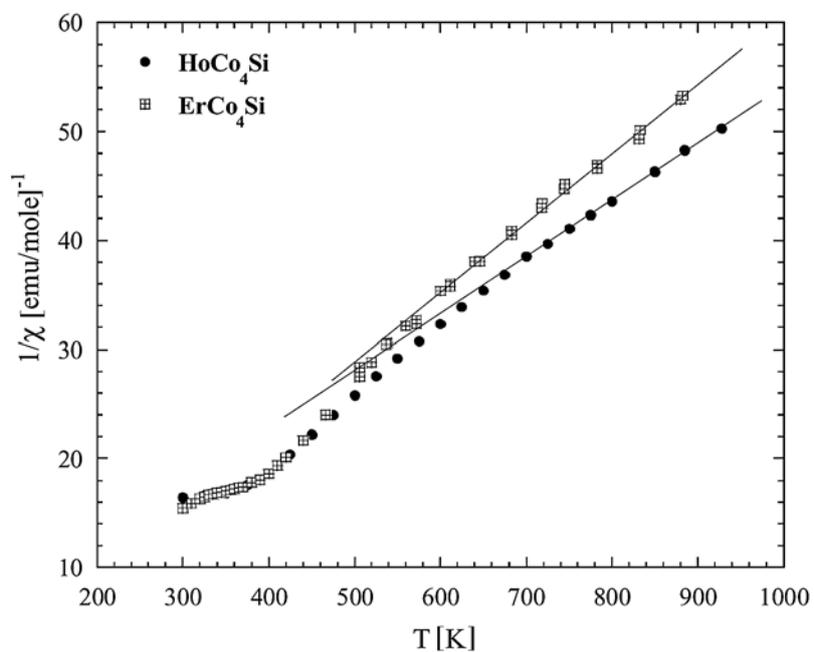

Fig. 4 – The temperature dependence of reciprocal susceptibility for HoCo$_4$Si and ErCo$_4$Si.

ordered magnetic moment, this leads to a mean magnetic moment per Co atom of about 1.3 μ_B, value much reduced comparison with the 1.8 μ_B known to be observed for the RCo_5 compounds. In order to better understand the magnetic behaviour of cobalt in this system, further studies (magnetisation and neutron diffractions) at low temperature are in progress. It is worth noting that, due to the very high Curie temperatures of the RCo_5 phases, very few experimental data are available on the paramagnetic domains.

Table 3

The Curie constants, effective magnetic moments and spontaneous magnetisation
of the RCo_4Si intermetallic compounds

R	C (RCo_4Si) (K·emu/mole)	μ_{eff} (Co) (μ_B/atom)	μ_{eff} (R^{3+}) (μ_B/atom)	M_s (μ_B/f.u.) $T = 4$ K
Tb	16.6	3.1(1)	9.7	4.4
Dy	18.4	3.0(1)	10.6	4.5
Ho	19.1	3.2(1)	10.6	4.3
Er	16.7	3.2(1)	9.6	3.8

CONCLUSIONS

Crystallographic and magnetic behaviours in the paramagnetic region of RCo_4Si (R = Gd, Tb, Dy, Ho, Er) phases have been studied. The crystalline structure has been refined from X-ray diffraction patterns using Cu Kα radiation. Curie temperatures were determined from the temperature variation of magnetisation in low magnetic field. The *M/H* field dependencies attest the absence of magnetic impurities above the Curie temperatures.

RCo_4Si compounds crystallise in the $CaCu_5$ type structure of the P6/mmm space group. The values of the *a* parameter differs less than 0.5% from those of RCo_5 compounds. The *c* parameter is little reduced by about 1.6% when Si is substituted for Co.

The significant reduction of the Curie temperature by 600÷670 K found in RCo_4Si intermetallic compounds in comparison with that of the RCo_5 compounds can be explained by the substitution of a 3*d* magnetic metals, Co, by nonmagnetic *p* elements and the (Co)*d* – (Si)*p* hybridisation. In the high temperature region, the reciprocal susceptibility was fitted by a linear law. In agreement with the additional law of susceptibility, we obtained the effective moment of cobalt assuming an effective rare earth moment as in R^{3+} free ions. The computing effective cobalt moment in RCo_4Si (R = Tb, Dy, Ho, Er) compounds are in good agreement with the effective cobalt moment previously obtained by Burzo in

$(Y_{1-x}Gd_x)Co_4Si$ compounds [16]. In order to establish the magnetic behaviour of cobalt in RCo_4Si, further magnetic studies are in progress in the low temperature region.

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