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The effect of silicon on the exchange interactions in $\text{Gd}_x\text{Ce}_{1-x}\text{Co}_4\text{Si}$ compounds

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Abstract

The $\text{Gd}_x\text{Ce}_{1-x}\text{Co}_4\text{Si}$ compounds with $x = 0, 0.2, 0.4, 0.6, 0.8$ and 1.0 crystallize in the hexagonal structure of the CaCu_5 type, with the space group $P6/mmm$. CeCo_4Si exhibits anomalously low values of the elementary cell volume as well as of the Curie temperature and the mean cobalt moment in the RCo_4Si series ($R = \text{rare earth or yttrium}$). All compounds exhibit a ferrimagnetic-type ordering. Band structure calculations using the *ab initio* tight-binding linear muffin tin orbital method in the atomic sphere approximation were performed for RCo_4Si , $R = \text{Ce, Gd}$. The computations provide evidence that the induced Ce moments are oriented antiparallel to the Co ones. The effect of Si and B atoms on the R–Co exchange interactions and on the magnetic behaviour of Co in $\text{RCo}_4\text{B/Si}$ compounds is discussed comparatively.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Previous studies have evidenced that the partial substitution for Co with non-magnetic elements, such as B, Al, C or Si, in RCo_5 compounds ($R = \text{rare earth or yttrium}$) produces significant changes of the magnetic and structural properties [1–5]. Cobalt atoms occupy two different crystallographic sites in RCo_5 -type structure: 2c—in the same plane with the R atoms—and 3g—in the plane containing only Co atoms.

Boron atoms substitute preferentially for Co from 2c sites, forming the $\text{R}_{n+1}\text{Co}_{3n+5}\text{B}_{2n}$ series, with $n = 0, 1, 2, 3, \dots, \infty$, which show similarities of structure and magnetic behaviour [6, 7]. Other metalloids such as C, Al, Ga, Si appear to substitute for cobalt atoms from 2c and 3g sites, the corresponding compounds preserving the CeCo_5 -type structure [8–10].

In the lanthanide series, cerium represents a special case. Due to the 4f states being energetically very close to the Fermi level, in cerium intermetallics the 4f hybridization with the conduction electron bands becomes important. This can lead to a configuration with

Table 1. Structural and magnetic data for $\text{Gd}_x\text{Ce}_{1-x}\text{Co}_4\text{Si}$ compounds.

x	a (Å)	c (Å)	V (Å ³)	T_c (K)	M_s (μ_B/fu)	M_{Co} (μ_B/atom)	M_{eff} (Co) (μ_B/atom)
0	4.8868	4.0253	83.2486	225	0.84	0.21	2.47
0.2	4.8924	4.0163	83.2536	301	0.78	0.53	2.65
0.4	4.9081	4.0048	83.5481	340	0.52	0.57	2.89
0.6	4.9216	3.9953	83.8084	381	0.32	0.96	3.02
0.8	4.9363	3.9695	83.7684	420	0.73	1.19	3.36
1.0	4.976 [10]	3.973 [10]	85.1941	470 [10]	1.88 [9]	1.28	3.51

non-integer electronic 4f occupation number, the corresponding intermediate valence systems being characterized by anomalous physical properties [11–13]. As a consequence, Ce based compounds are of special interest. It is known that Ce magnetism is sensitive to the local symmetry and chemical environment. Previously we investigated the magnetic behaviour of the $\text{Gd}_x\text{Ce}_{1-x}\text{Co}_4\text{B}$ system [14]. The aim of the present study is to investigate the magnetic properties of $\text{Gd}_x\text{Ce}_{1-x}\text{Co}_4\text{Si}$ compounds and to analyse the influence of the increased number of p electrons of the substituting metalloid (Si) on the exchange interactions and on the Ce magnetic behaviour.

2. Experimental details

Polycrystalline samples were prepared by melting the constituent elements, with a purity higher than 99.99%, in an arc furnace in an argon atmosphere. To compensate for the weight loss of rare earth during melting and thus to avoid the formation of other phases with higher Curie temperatures, a slight excess of rare earth was added. Each sample was remelted several times in order to ensure homogeneity. After preparation the compounds were sealed in quartz tubes under vacuum and thermally treated at 1000 °C for a week.

The crystal structure was investigated using the x-ray diffraction technique. Magnetic measurements were performed in the temperature range 1.5–800 K and in fields of up to 10 T, using the extraction method. The spontaneous magnetizations M_s , were obtained from the magnetization isotherms by extrapolation to zero field of the measured values of the magnetization. The Curie temperatures were determined from the temperature dependence of the magnetization in low field (0.02 T). In the paramagnetic regime, the possible presence of some small quantities of magnetic ordered impurity could alter the magnetic susceptibility, χ . In order to avoid this, accurate χ values were obtained from their field dependences by extrapolating at $H^{-1} \rightarrow 0$.

3. Experimental results

$\text{Gd}_x\text{Ce}_{1-x}\text{Co}_4\text{Si}$ compounds crystallize in a hexagonal structure of the CaCu_5 type, having the space group $P6/mmm$. It is possible that the Si atoms substitute randomly for Co from 2c and 3g sites. The a and c lattice parameter values are presented in table 1. The elementary cell volume increases with the Gd content.

The first magnetization isotherms for $\text{Gd}_x\text{Ce}_{1-x}\text{Co}_4\text{Si}$ compounds with $x \leq 0.4$ exhibit a step-like transition when increasing the external field; see figure 1. These transitions could be associated with an internal field, which blocks the rotation of magnetization in the domains. The saturation of magnetization is not attained in fields of up to 10 T at low temperatures. Therefore our experimental values of the magnetization at 4.2 K are somewhat lower than the real ones. The temperature dependence of the spontaneous magnetization, represented in

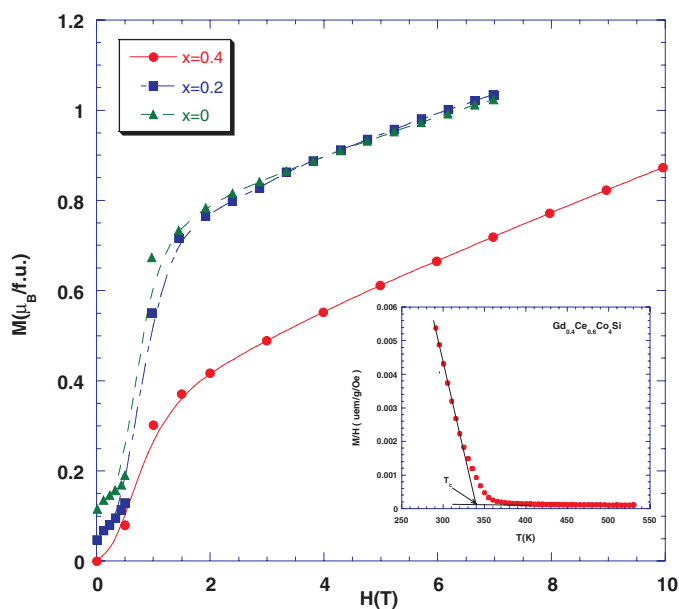


Figure 1. The first magnetization isotherm at 10 K, for $\text{Gd}_x\text{Ce}_{1-x}\text{Co}_4\text{Si}$ compounds, with $x \leq 0.4$. Inset—the Curie temperature for $\text{Gd}_{0.4}\text{Ce}_{0.6}\text{Co}_4\text{Si}$, determined from the temperature dependence of the magnetization at 0.02 T.

figure 2, is characteristic of a ferrimagnetic ordering over the whole composition range. In the case of CeCo_4Si , due to the hybridization of Ce 4f states with the Co 3d band, a small magnetic moment is induced on Ce atoms, oriented antiparallel to the Co one, as evidenced below by band structure calculations. This explains the resemblance of the M versus T curve to one characteristic of a ferromagnetic compound.

From the spontaneous magnetization values at 4.2 K (table 1), we estimated the mean Co moments, M_{Co} , using a two-sublattice ferrimagnet model, where the magnetic moments of the Gd^{3+} ions (considered as $7 \mu_{\text{B}}$) are oriented antiparallel to the Co moments. The M_{Co} values become higher with the Gd content (table 1). As Ce is replaced by Gd, due to the Gd 4f localized moments the exchange interactions in the system increase, a fact confirmed by the trend of the Curie temperatures, T_{C} (table 1). The study of $(\text{Gd}_x\text{Y}_{1-x})_{n+1}\text{Co}_{3n+5}\text{B}_{2n}$ compounds, with $n = 1, 2, 3$, revealed that a small Co moment is induced by the exchange field, which increases with the Gd content [7]. The same mechanism could explain the trend of M_{Co} in the $\text{Gd}_x\text{Ce}_{1-x}\text{Co}_4\text{Si}$ series.

Above the Curie temperatures, the reciprocal susceptibility of the compounds follows a Néel-type law; figure 3. Again, in the case of CeCo_4Si , due to the small induced Ce moment, the $\chi^{-1}(T)$ behaviour resembles a ferromagnetic-type one, described by a modified Curie–Weiss law, $\chi = \chi_0 + C(T - \theta)^{-1}$, where χ_0 is a Pauli-type contribution to the susceptibility, θ is the paramagnetic Curie temperature and C is the Curie constant. From the experimental curves we determined the Co contribution to the Curie constants. The effective cobalt moments, $M_{\text{eff}}(\text{Co})$, increase significantly with composition, from $2.47 \mu_{\text{B}}/\text{atom}$ ($x = 0$) to $3.51 \mu_{\text{B}}/\text{atom}$ ($x = 1$); table 1.

4. Density of states

Band structure calculations for CeCo_4Si and GdCo_4Si compounds were performed; they were based on the local density functional approximation (LDA) and employed the tight binding

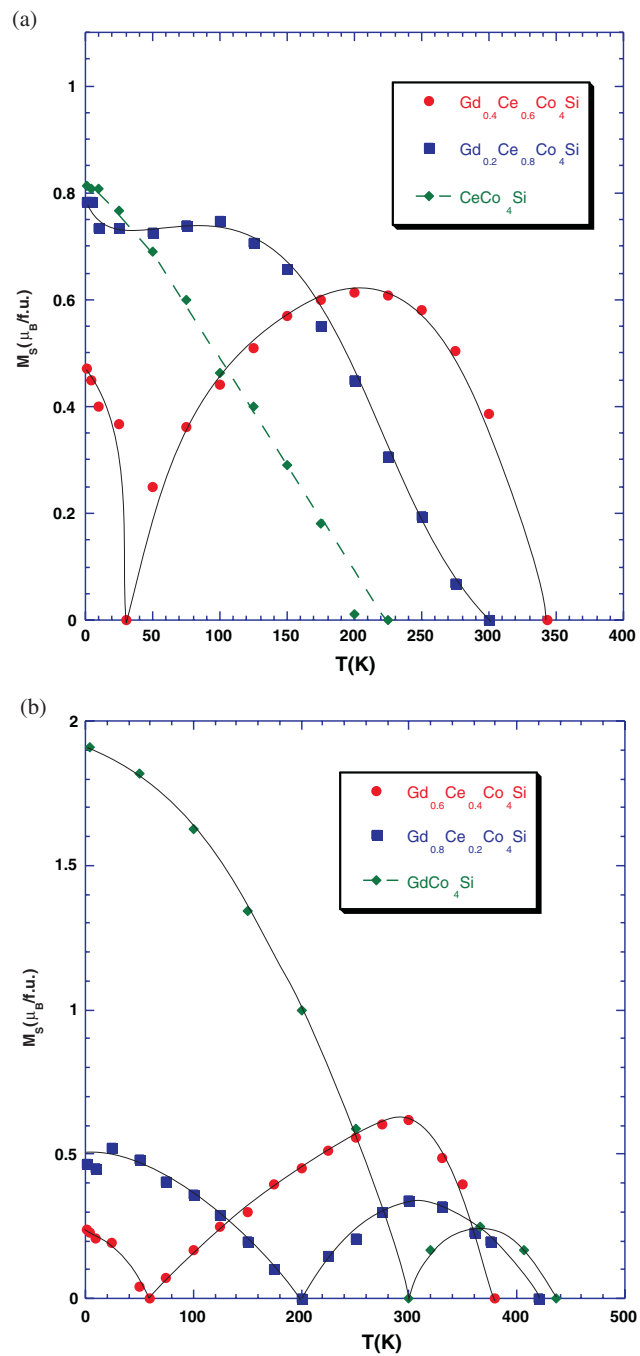


Figure 2. The temperature dependence of the spontaneous magnetization, for $x = 0, 0.2$ and 0.4 (a) and for $x = 0.6, 0.8$ and 1 (b).

linear muffin-tin orbital method in the atomic sphere approximation [15, 16] to solve the Kohn–Sham equations. The exchange–correlation potential was approximated by the parametrization of von Barth and Hedin [17].

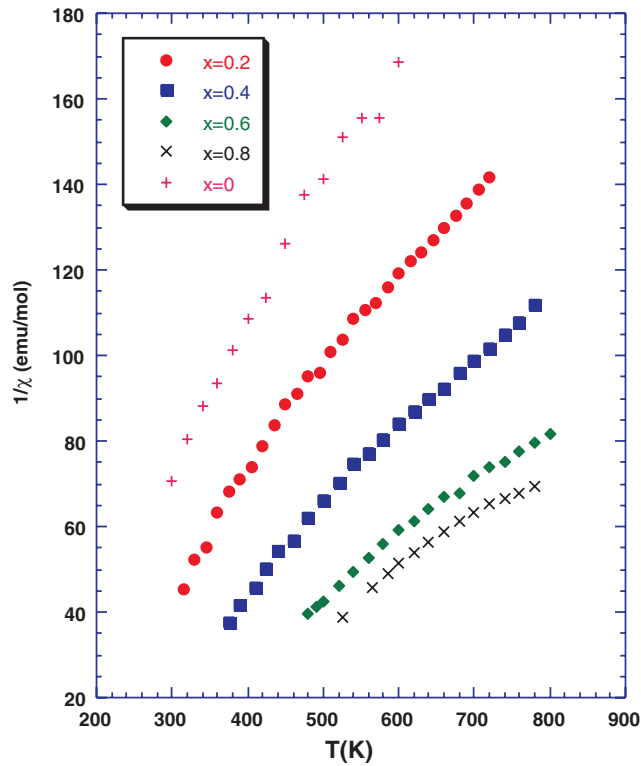


Figure 3. The temperature dependence of the reciprocal susceptibilities in the $\text{Gd}_x\text{Ce}_{1-x}\text{Co}_4\text{Si}$ system.

The spin-polarized computations were performed for the experimental lattice parameters $a = 4.8868 \text{ \AA}$ and $c = 4.0253 \text{ \AA}$ obtained for CeCo_4Si and using the previously reported values $a = 4.9533 \text{ \AA}$ and $c = 3.9200 \text{ \AA}$ for GdCo_4Si [9]. Relativistic corrections were included, without the spin-orbit coupling. The energy eigenvalues were determined using 216 k points in the irreducible part of first Brillouin zone. Two cases were considered for RCO_5 ($R = \text{Ce}$ and Gd), corresponding to Si substituting for Co from 2c sites and respectively from 3g sites. The 4f orbitals were considered as core states for Gd and as band states for Ce. Some values of the atomic Wigner-Seitz radii used in the calculations for CeCo_4Si are 3.433 au for Ce, 2.677 au for Co 2c, 2.645 au for Co 3g and 2.631 au for Si placed in a Co 2c site. In the case of GdCo_4Si , where the Si atom occupies a Co 3g position, the radii are 3.545 au for Gd, 2.616 au for Co 2c, 2.611 au for Co 3g and 2.627 au for Si. Calculations were performed for CeCo_5 and GdCo_5 using the same approach to enable comparison and discussion of the theoretical results.

The contributions to the DOS from R, Co and Si atoms, as well as the total DOS, are presented in figure 4 for CeCo_4Si and figure 5 for GdCo_4Si . The computed values of the atomic magnetic moments and of the magnetization per formula unit are presented in table 2. The 3d spin down sub-band of Co atoms at 2c and 3g sites becomes almost entirely occupied for $R = \text{Gd}$, evidencing that GdCo_4Si almost satisfies the criterion for a strong ferromagnet. The theoretical values of the spontaneous magnetization, M_s^{LMTO} , are higher by $\sim 1 \mu_B$ for CeCo_4Si and $\sim 1.7 \mu_B$ in the case of GdCo_4Si . The observed discrepancy is explained by saturation of magnetization not being reached in fields of up to 10 T. Thang *et al* [10] have

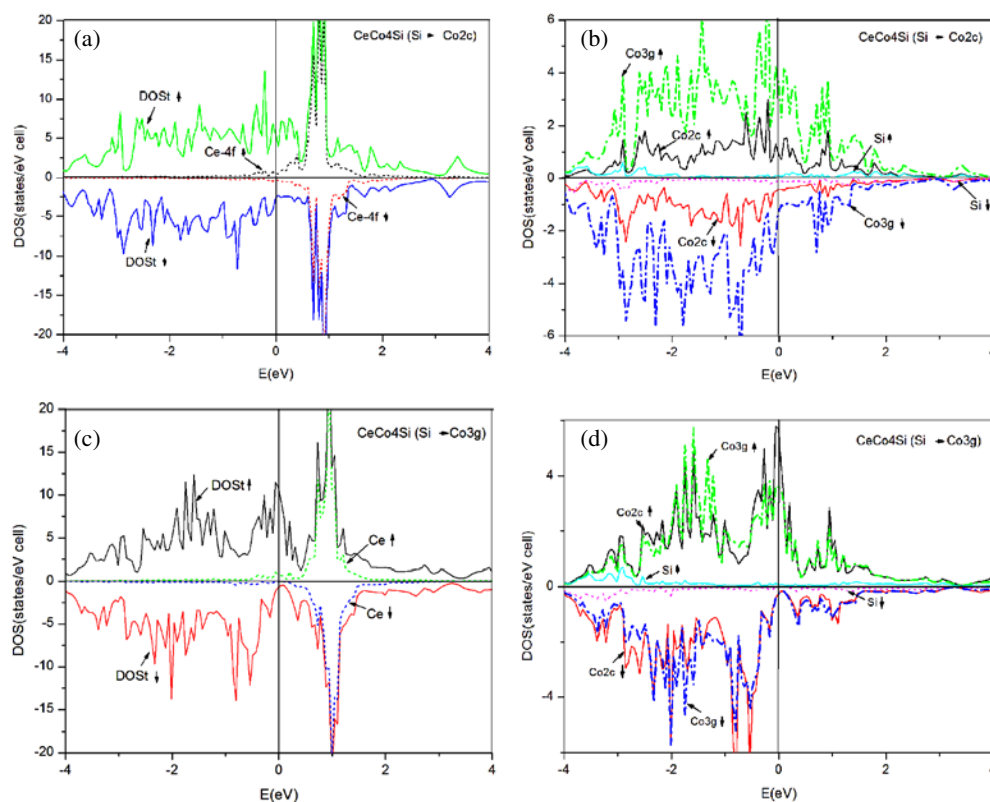


Figure 4. The total DOS and DOS contributions of R, Co and Si atoms in CeCo_4Si , with Si in the Co 2c site ((a) and (b)) and in the Co 3g site ((c) and (d)).

Table 2. Theoretical values of the atomic magnetic moment and of the total moment/formula unit, in RCO_5 and RCO_4Si compounds, with R = Ce and Gd.

Atom	CeCo_5	CeCo_4Si Si → 2c	CeCo_4Si Si → 3g	GdCo_5	GdCo_4Si Si → 2c	GdCo_4Si Si → 3g
	R	-0.653	-0.245	-0.277	-7.530	-7.375
Co 2c	1.206	0.634	0.639	1.479	1.214	0.954
Co 3g	1.231	0.575	0.498	1.414	0.840	0.833
Si	—	-0.018	-0.030	—	-0.05	-0.04
M_s^{LMTO} ($\mu_B/\text{f.u.}$)	5.453	2.096	1.969	-0.327	-3.688	-3.800

reported an experimental value of $M_s = 2.76 \mu_B$ for GdCo_4Si , obtained from measurements on free powder samples. Recent studies of the neutron diffraction of RCO_4Si compounds indicate a preference of Si for the 3g crystallographic positions [18]. A similar behaviour was previously inferred for Al in GdCo_5 [19] and for Al and Ga in CeCo_5 [8].

5. Discussion

It is currently accepted that the 4f–3d interactions in rare earth–transition metal based alloys involve intra-atomic 4f–5d exchange, 3d exchange and 3d–5d interactions [20]. A systematic

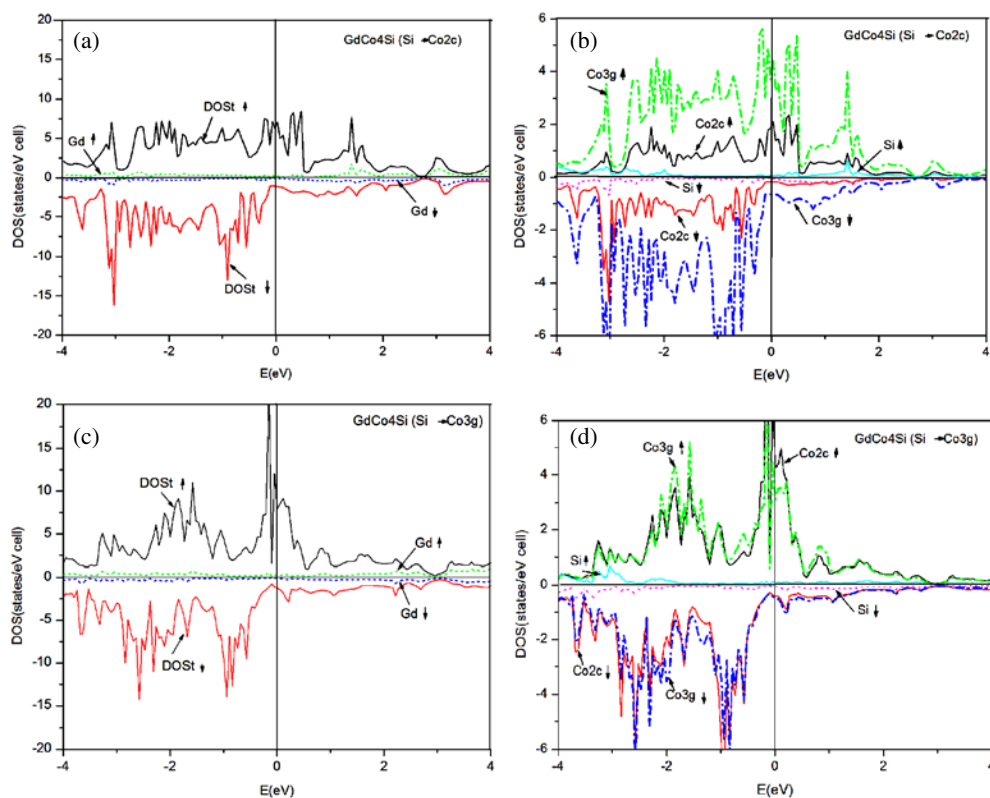


Figure 5. The total DOS and DOS contributions of R, Co and Si atoms in GdCo_4Si , with Si in the Co 2c site ((a) and (b)) and in the Co 3g site ((c) and (d)).

analysis of the magnetic properties of R–T based compounds revealed that the variable degree of 3d–5d hybridization essentially determines the variation in the 3d–4f exchange interactions [21]. The induced 5d moment at the R site consists of two contributions: an induced polarization due to exchange interactions with 3d bands and a term proportional to the de Gennes factor, resulting from the local 4f–5d exchange [22]. For RCO_5 compounds and for the compounds derived from these, such as GdCo_4M , where $\text{M} = \text{B}$ or Si , the latter term is $\sim 0.23 \mu_{\text{B}}$. The band structure calculations yield a smaller induced Gd 5d moment for GdCo_4Si compared to GdCo_4B . Thus the contribution arising from 3d–5d interaction is diminished although the mean Co moment in GdCo_4Si is higher than in GdCo_4B . Also, the induced moment on the Ce site in CeCo_4Si is lower than that in CeCo_4B . Si has an extra p electron in the outer shell, compared to B. As a result, it is expected that the effect of the 2p electrons on the 3d–5d hybridization will be more pronounced in the case of Si compounds.

Compared to other compounds of the RCO_4Si type [10], CeCo_4Si exhibits, like CeCo_4B in the homologous series, anomalies of the structural properties, as well as of the magnetic characteristics. The a lattice parameter and the elementary cell volume have minimum values, deviating from the monotonically decreasing curves (figure 6) corresponding to the lanthanide series, while the c constant is maximum. The Curie temperature, the spontaneous magnetization and the mean cobalt moment of CeCo_4Si have the minimum values in the RCO_4Si series.

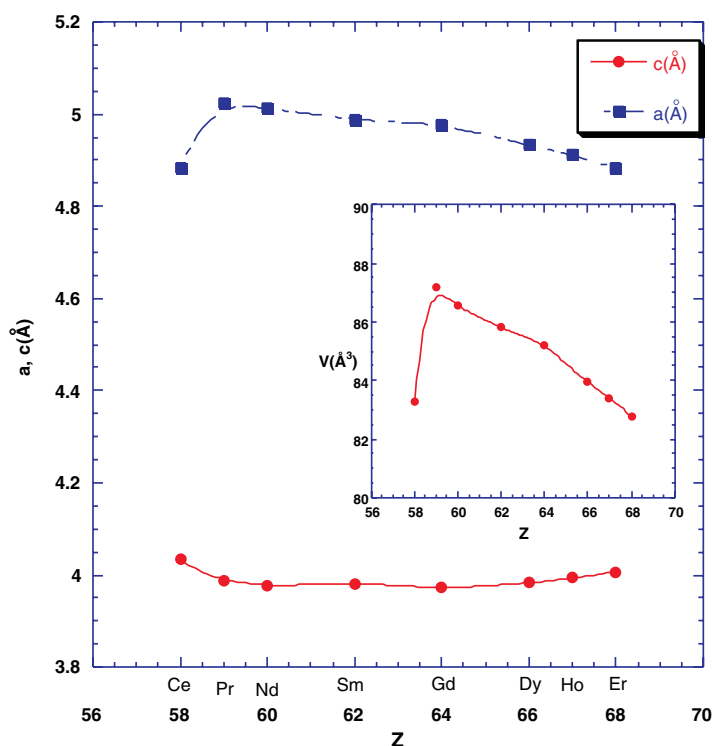


Figure 6. Lattice parameters and the elementary cell volume for RCo₄Si compounds. For R \neq Ce, the a and c values are from [10].

The origin of this anomalous behaviour is the delocalization of the cerium 4f states. Thus Ce does not fit the standard rare earth model. In consequence, there is an additional 3d–4f hybridization, besides the 3d–5d one, as evidenced by the band structure calculations. Since the separation in energy between the centres of gravity of the Ce 4f and Co 3d ($2c$ or $3g$) \uparrow (minority) bands is lower than that between the Ce 4f and Co 3d \downarrow ones, the Ce 4f–Co 3d \uparrow hybridization is stronger, leading to the partial filling of the minority spin 3d band and to an anomalous decrease of the Co moment. The antiparallel orientation of the 3d (Co) and the induced R moments arise from the spin dependence of the hybridization strength, as previously evidenced in the case of CeCo₅ [23].

As pointed out above, Si 2p electrons reduce the 3d–5d interactions and the magnitude of the Co magnetic moment via 3d–2p hybridization. The 5d R induced polarization and the Co magnetic moments are lower in RCo₄Si than in RCo₅ and RCo₄B (R = Ce and Gd). Moreover, the Curie temperatures in Gd_{*x*}Ce_{1–*x*}Co₄Si compounds are lower than in the homologous series, Gd_{*x*}Ce_{1–*x*}Co₄B [14, 24], but the mean Co moment values are higher in the Si series. A similar behaviour is observed when comparing the experimental data for Gd_{*x*}Y_{1–*x*}Co₄B and Gd_{*x*}Y_{1–*x*}Co₄Si [25, 9]. For R = Gd a difference in Co mean moment of 0.3 μ_B is obtained experimentally (in the absence of saturation). The LMTO calculations yield a difference of the same magnitude, increasing from ~ 0.1 for R = Ce to ~ 0.2 for R = Gd.

Duc and Givord [26], in a previous analysis of Gd_{*m*}Co_{*n*}B_{*k*} compounds, evidenced the influence of the 2p B electrons on the exchange interactions and on the Co moment, by computing the microscopic exchange coupling parameter, A_{RT} . They showed that A_{RT}

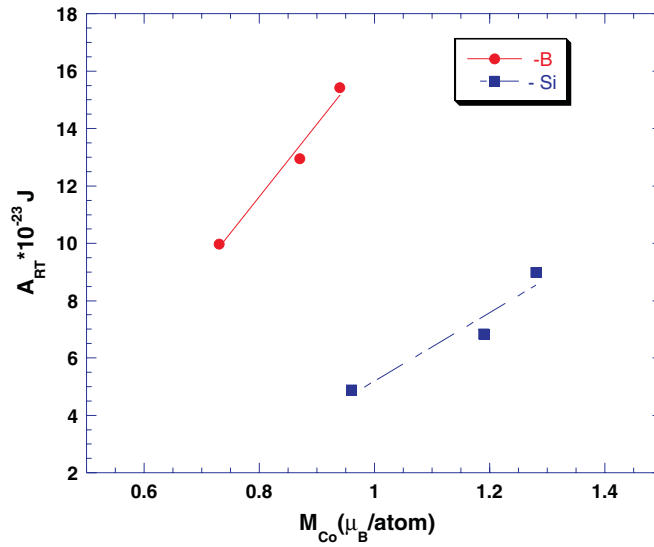


Figure 7. The exchange coupling parameter in $Gd_xCe_{1-x}Co_4M$ compounds, with $x \geq 0.6$ and $M = B$ and Si .

diminishes with the relative boron content (k/n), following the same trend as the mean magnetic moment [26, 27]. On the basis of the results of Aoki and Yamada [28], they conclude that the B 2p electrons reduce the 3d band splitting, and hence the Co moment and the 3d–5d hybridization, since the density of states at the Fermi level is reducing.

We evaluated the A_{RT} parameter for the $Gd_xCe_{1-x}Co_4M$, $M = B$ and Si , compounds with $x \geq 0.6$, where the anisotropy associated with the presence of Ce was neglected. The expression for the microscopic exchange coupling parameter, A_{RT} , is given by the expression below [26]:

$$\left(\frac{A_{RT}}{k_B}\right)^2 = \frac{9(T_C - T_R)(T_C - T_T)}{4Z_{RT}Z_{TR}G_R G_T} \quad (1)$$

where T_C is the Curie temperature of the compound, obtained experimentally. The rare earth contribution to the Curie temperature, T_R , for a given composition x was obtained by linear interpolation between the Curie temperatures of $GdNi_2$ (76 K) and $CeNi_2$ (Pauli paramagnet). The transition metal contribution to the Curie temperature, T_T , was taken as the Curie temperature of YCo_4B for $Gd_xCe_{1-x}Co_4B$ and that of YCo_4Si [9] for $Gd_xCe_{1-x}Co_4Si$ compounds, with $x = 0.6, 0.8$ and 1 . Z_{TR} denotes the average number of R nearest neighbours of a Co atom and for both systems was considered to be 3.6 [26]. Z_{RT} represents the number of nearest T neighbours of an R atom. Since in the exchange coupling formalism $N_T Z_{TR} = N_R Z_{RT}$, where N_T and N_R are the numbers of T and R atoms per fu, for both systems Z_{RT} is considered to be 15. G_R is the rare earth de Gennes factor and $G_T = M_{\text{eff}}(\text{Co})/4$, where M_{eff} is the effective paramagnetic moment of Co, is the corresponding factor for Co. The exchange coupling parameter as a function of the mean cobalt moment, in the two series, for $x \geq 0.6$, is illustrated in figure 7. This clearly shows a more pronounced decrease of the R–Co exchange interactions in the Si system, following the trend of the Curie temperatures in the two series. The slightly higher mean Co values, of the order of $0.2 \mu_B$ for $x \geq 0.6$ in the Si series compared to the B one, could be explained by taking into account the B/Si atom distribution. In the case of an ordered substituent distribution, as in RCo_4B -type compounds,

a higher relative number of Co–2p element bonds, compared to the Co–Co ones, than in the case of a non-ordered occupation is ensured.

Another factor that could account for the differences in mean Co moment and in band structure is the difference of the atomic 3p energy levels of the substituents, as evidenced in $Y(\text{Co}, \text{Al})_2$ and $Y(\text{Co}, \text{Si})_2$ compounds [28].

6. Concluding remarks

In the present paper we have studied the crystallographic and magnetic properties of the $(\text{Gd}, \text{Ce})\text{Co}_4\text{Si}$ compounds. An anomalous structural and magnetic behaviour is observed for CeCo_4Si , characteristic of intermediate valence systems. In CeCo_5 and CeCo_4B , due to additional 4f–3d hybridization, the induced moments per cerium atom are higher than the ones induced on Gd atoms; however, in CeCo_4Si the opposite is found. This may be due to a stronger Ce 4f mixing with p states of Si, which also reduces the Ce moment.

Also, a stronger effect of Si 2p electrons on the 3d–5d hybridization is evidenced, compared to the boron case, which results in reduced R–Co exchange coupling.

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