Magnetic properties and electronic structures of GdCo$_{3-x}$Si$_x$ compounds

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Abstract

Magnetic measurements and band structure calculations were performed on GdCo$_{3-x}$Si$_x$ system with $x \leq 0.3$. The experimentally determined magnetizations are in rather good agreement with those obtained from band structure calculations. The composition dependence of cobalt moments, at various lattice sites, are analyzed in correlation with the effects of Co 3d–Si 3p bands hybridization.
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Keywords: Intermetallics; Electronic band structure; Magnetic measurements

The RCo$_3$ compounds, where R is a rare-earth or yttrium, crystallize in a rhombohedral type lattice having $R\bar{3}m$ space group. In this lattice, the R atoms occupy 3a and 6c sites, while cobalt atoms are distributed on 3b, 6c and 18h positions. Due to different local environments, the cobalt magnetic moments are dependent on lattice sites [1]. The RCo$_3$ compounds show interesting magnetic properties, particularly associated with a wide range of their stoichiometry. Field induced transitions were also shown in YCo$_3$ or diluted R$_{1-x}$Y$_x$Co$_3$ compounds [2,3]. It is also of interest to analyze the effect of cobalt substitutions by nonmagnetic elements on the magnetic properties of RCo$_3$ compounds. Previously, we showed that the mean cobalt moments in GdCo$_{3-x}$Al$_x$ system is strongly dependent on composition [4]. As an on going work on this matter we studied the magnetic properties of GdCo$_{3-x}$Si$_x$ system. In addition to magnetic measurements, band structure calculations were also performed. These give additional informations on cobalt moments, at various sites, as well as on Gd(5d) band polarizations.

The GdCo$_{3-x}$Si$_x$ samples with $x \leq 0.30$ were prepared by melting the constituent elements in an arc furnace. These were remelted several times in order to ensure a good homogeneity. The compounds were thermally treated at 850 °C for one week. The X-ray analyses show the presence of a rhombohedral type lattice in all the studied composition range. The c lattice constants decrease little, while a parameter remains practically constant when increasing silicon contents.

The Rietveld refinement was performed with a TOPAS program version 2.0 in case of Gd$_9$Co$_{25}$Si$_2$ sample. The silicon is mainly located in 18h sites. The local environment analysis shows that the smaller distances between next neighboring cobalt atoms, of 2.49 Å, are characteristic for both Co 18h and Co 3b sites. Thus, from dimensional consideration the silicon having smaller radius will prefer those sites. The above statement is in agreement with the analysis of atomic ordering in ErFe$_{3-x}$Ni$_x$ system [5] which showed that the smaller atoms prefer 18h sites.

Magnetic measurements were performed in the temperature range 4.2–1000 K and fields up to 9.5 T. The saturation magnetizations, M_S, were obtained from magnetization isotherms according to approach to saturation law $M = M_S(1 - b/H)$, where by b is denoted the coefficient of magnetic hardness. Above the Curie points, the susceptibilities, χ, were determined from their field dependences, according to Honda–Arrott plot, $\chi_m = \chi + dM'_S H^{-1}$ by extrapolating the measured values χ_m at $H^{-1} \rightarrow 0$. By d is denoted a presumed impurity content and M'_S is their saturation magnetization. By this method any influence of possible presence of magnetic ordered impurities, on χ values, is eliminated. The experimental data show that, when exist, the magnetic impurity content is below 0.1%.

Band structure calculations were carried out by using the ab initio tight binding linear muffin thin orbital method in the atomic sphere approximation (TB–LMTO–ASA), within the

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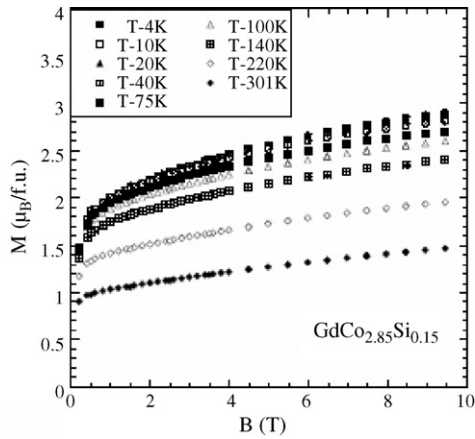*E-mail address:* rote@phys.ubbcluj.ro (R. Tetean).

Fig. 1. Magnetization isotherms for the compound with $x = 0.15$.

LDA and the LDA + U [6,7] approaches. The detailed procedure of calculation was described elsewhere [8]. In the framework of local density approximation (LDA), the total electronic potential is the sum of external, Coulomb and exchange-correlation potentials [9]. The functional form of the exchange correlation energy, in the present work, was the free electron gas parameterization of Von Barth and Hedin [10]. Relativistic correlations were included without the spin–orbit coupling in the LDA + U method. The values of $U = 6.9$ eV and $J = 0.9$ eV were used for gadolinium [6]. Convergence was reached within 10^{-6} Ry and a Brillouin mesh of $6 \times 6 \times 2k$ points for the supercells of Gd_9Co_{27} types, having nine times greater unit cell than that of $GdCo_3$. The Rietveld analysis showed that Si is mainly located in 18h sites. Accordingly, in performing band structure calculations, one or two silicon atoms in the Gd_9Co_{27} type cell were located in 18h sites. In addition, we had performed band structure calculations for the sample $Gd_9Co_{26}Si$ in which Si was presumed to be located also in 3b and 6c sites.

Some magnetization isotherms for the sample with $x = 0.15$ are plotted in Fig. 1. One can see that the saturation is not attended even in 9.5 T external magnetic field. The same behavior was also shown for all compounds. The thermal variations of saturation magnetizations, M_S, are plotted in Fig. 2. The M_S values, at 4.2 K, increase when the silicon content is
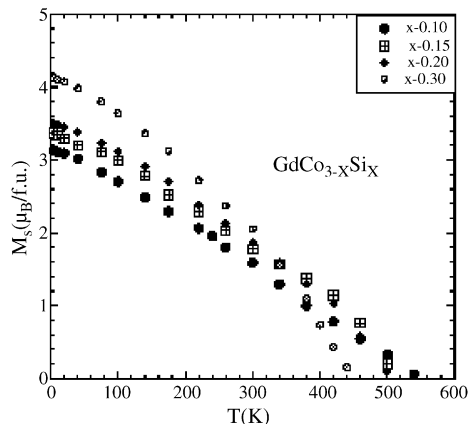

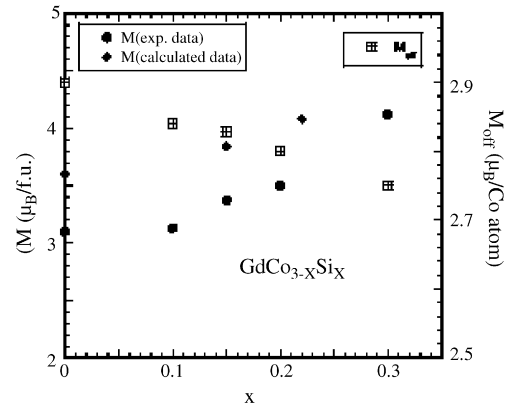Fig. 2. Thermal variations of saturation magnetizations.

Fig. 3. Composition dependences of the saturation magnetizations per formula unit, and mean effective cobalt moments.

higher, as expected for an antiparallel alignment of Gd and Co moments. We note that the determined magnetization in $GdCo_3$, of $\cong 3.00$ μ_B/f.u., is very close to the value reported by high field measurements on $GdCo_3$ single crystal ($\cong 3.05$ μ_B/f.u.) [11]. Assuming that the gadolinium moment is given by $g_J J = 7$ μ_B value, the mean cobalt moments, M_{Co}, were determined. The M_{Co} values decrease from 1.24 μ_B/atom ($x = 0$) to 1.10 μ_B/atom ($x = 0.3$).

In paramagnetic range the reciprocal susceptibilities follow hyperbolic law of Néel type [12]. From the characteristic linear dependences at high temperatures, we have determined the Curie constants, C. Assuming that the Curie constant of gadolinium is the same as that of Gd^{3+} free ion, the contributions of cobalt atoms, C_{Co}, to C values and the effective cobalt magnetic moments, $M_{eff}(Co)$, respectively, were determined. The $M_{eff}(Co)$ values decrease from 2.90 μ_B/atom ($x = 0$) to 2.75 μ_B/atom ($x = 0.3$) (Fig. 3). The ratio r between the number of spins, S_p, determined from mean effective moments, and from mean saturation cobalt moments, S_0, increases little from 1.67 ($x = 0$) to 1.75 ($x = 0.3$). These values suggest no much degree of itinerancy.

The projected densities of states for Gd_9Co_{27} and $Gd_9Co_{25}Si_2$ with Si located in 18h sites are plotted in Fig. 4. The magnetic moments of constituent atoms were determined either within the LDA 4f frozen core calculations or with the LDA + U method considering a Gd 4f band description. The values thus computed agree rather well. In case of $GdCo_3$ compound, the cobalt moments follows the sequence $M_{Co}(6c) > M_{Co}(3b) > M_{Co}(18h)$. This sequence is similar to that determined by neutron diffraction study on YCo_3 [1] or $Er_{1-x}Y_xCo_3$ [13]. It has been pointed, in YCo_3, that the highest Co magnetic moment, Co(6c), is associated with the crystallographic site having the least Y near neighbors while the lowest value is associated with those having the most Y next neighbors (18h) [1]. Replacing Y by Gd, due to 4f–5d–3d exchange interaction an additional moment is induced by gadolinium on cobalt sites. Consequently, the cobalt moments increase as compared with the values determined in YCo_3, particularly for sites having the greatest number of Gd atoms as nearest neighbors. Thus, the Co moments for 18h site increase by $\cong 1.00$ μ_B and for 6c sites
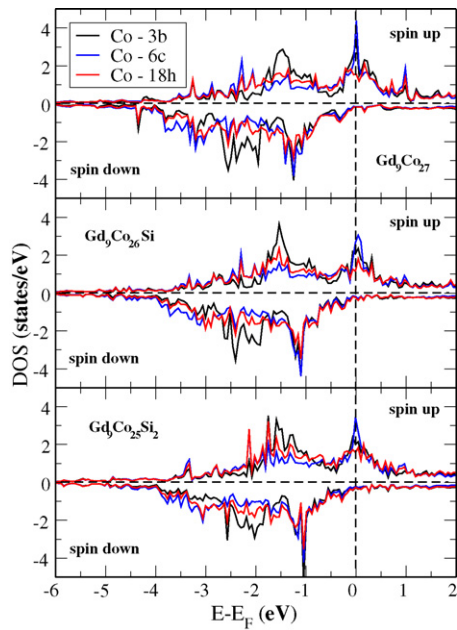
Fig. 4. The projected densities of states for Co sites in $Gd_9Co_{27-x}Si_x$ compounds.

Table 1
Data obtained from band structure calculations (LSDA + U) for the $GdCo_{3-x}Si_x$ compounds with Si located in 18h site

x	Magnetic moment (μ_B/atom)						
	Gd(3a)		Gd(6c)		Co		
	4f	5d	4f	5d	3b	6c	18h
0.00	−7.00	−0.53	−7.00	−0.54	1.24	1.35	1.21
0.11	−7.00	−0.46	−7.00	−0.49	1.24	1.35	1.14
0.22	−7.00	−0.45	−7.00	−0.48	1.12	1.27	1.13

5d band polarization. We have calculated also the contribution of 5d(4d)–3d exchange to 5d(4d) band polarizations in $LuCo_3$ and YCo_3 compounds where both Lu and Y are not magnetic. A value of $\cong 0.28\,\mu_B$ was obtained. Admitting, in the first approximation as additive, the local 4f–5d contribution for R 5d band polarization is $\cong 0.25\,\mu_B$. We showed already [15] that the last contribution is not dependent on the substitution performed on transition metal sites. Thus, the decrease of resulting Gd 5d band polarizations (Table 1) can be attributed, for given Gd site, to the decrease of the number of Co neighboring atoms as well as their moments as results of substitution effects.

We conclude that the experimentally determined magnetizations are rather well described by band structure calculations. The variations of cobalt moments, at various sites, when substituting cobalt by silicon can be attributed to Co 3d–Si 3p hybridizations effects. The decrease of Gd 5d band polarizations when replacing Co by Si is due to the diminution of the short range 5d–3d exchange interactions as result of substitutions.

by $0.56\,\mu_B$ showing the stronger effect of 4f–5d–3d exchange interaction on cobalt sites having the greatest number of Gd as near neighbors.

We had analyzed also, by using band structure calculations, the effect of silicon substitution on 6c and 3b cobalt sites in $Gd_9Co_{26}Si$ sample. The magnetic moment per formula unit, more close to experimental data, was obtained in case of cobalt substitution in 18h sites in agreement with structural data. The computed magnetizations per formula unit, even when Si substitute Co in 18h sites, are higher by $\cong 0.5\,\mu_B$/f.u. than those experimentally determined. This difference is generally characteristic for near all rare-earth intermetallic compounds and can be related with difficulties in obtaining saturation magnetizations.

The Gd(5d) band polarizations are parallely oriented to 4f moments and decrease little when increasing Si content. When replacing Co by Si, there is a hybridization of Co 3d and Si 3p states and thus the exchange splittings of Co 3d bands are modified. The centers of gravity for Co 3d bands, for all Co sites are strongly shifted toward Fermi level, while the position of center of gravity of Si 3p band is only little modified. For $Gd_9Co_{26}Si$ compound there is a stronger hybridization of Co 3d(18h)↓ subband with Si 3p one, their centers of gravity being rather close. Thus, the Co 3d(18h) moment is more affected for Si substitution (Table 1).

The exchange interactions in the present system can be described by the 4f–5d–3d model [14]. There are local 4f–5d exchange interactions as well as 5d–3d short range interactions with neighboring Co atoms to the Gd one. Both contribute to the

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