ELSEVIER

Journal of Alloys and Compounds 323–324 (2001) 490–493

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

Magnetic properties and electronic structures of $RCo_{2-x}Si_x$ (R=Gd, Y) compounds

E. Burzo[a,*], R. Tetean[a], Zs. Sarkozi[a], L. Chioncel[a], M. Neumann[b]

[a]*Faculty of Physics, Babes-Bolyai University, Str. M. Kogalniceanu Nr. 1, Cluj-Napoca, RO-3400, Romania*
[b]*Institute of Physics, University of Osnabrück, D-49069 Osnabrück, Germany*

Abstract

Magnetic measurements and band structure calculations were performed on $YCo_{2-x}Si_x$ and $GdCo_{2-x}Si_x$ systems. For the $YCo_{2-x}Si_x$ exchange enhanced paramagnets the magnetic susceptibilities have maxima and at temperatures $T>T^*$ a Curie–Weiss type behavior is evidenced. The effective cobalt moments decrease when silicon content increases. This fact was attributed to p–d hybridization effects as evidenced from band structure calculations. The magnetic behavior of cobalt was analyzed in spin fluctuations model. The saturation moments at 4.2 K in $GdCo_{2-x}Si_x$ system are in agreement with those obtained from band structure calculations. The effective cobalt moments in $GdCo_{2-x}Si_x$ compounds are smaller than those determined in $YCo_{2-x}Si_x$ system. This fact was attributed to partial quenching of spin fluctuations by internal field.

Keywords: Rare earth compounds; Magnetic properties; Electronic structures

1. Introduction

In a previous paper [1] we showed that the magnetic susceptibilities, χ, of strong exchange enhanced paramagnets, such as YCo_2 or $LuCo_2$, at $T=15$ K, follow a T^2 dependence as predicted by paramagnon model [2]. The χ values increase with temperature, show maxima and then decrease. At $T>T^*$, where T^* is a characteristic temperature for a given system, the magnetic susceptibilities follow Curie–Weiss type dependencies. The effective cobalt moments, in the above compounds, are close to that of Co^{2+} ion considering only spin contribution. The above behavior is typical for a spin-fluctuations system [3,4].

Michels et al. [5] studied the magnetic properties of $YCo_{2-x}Si_x$ compounds at $T<380$ K. It is concluded that the substitution of Si for Co can lead to susceptibility enhancement factors of 3–6. Because of magnetic impurities no reliable data were obtained in the low temperature range. Later on, Duc [6] concluded that by partial substitution of Co by Si, the ordering temperatures are almost constant for $R(CoSi)_2$ systems with R=Gd, Tb and Dy, whereas a reduction of 3d magnetic moment is observed.

In this paper we analyze to what extent the magnetic behavior of RCo_2 (R=Y or Gd) is changed when cobalt is replaced by silicon. We therefore analyzed the magnetic properties of $YCo_{2-x}Si_x$ and $GdCo_{2-x}Si_x$ systems over a large temperature range. In addition, band structure calculations were performed and correlated with experimental data.

2. Experimental

The $RCo_{2-x}Si_x$ (R=Y or Gd) compounds were prepared by levitation method in purified argon atmosphere. A small excess of rare-earth (~1%) was used in order to compensate for loss by evaporation during the melting. The samples were heat treated in vacuum at 1000°C for 5 days. The X-ray analyses show the presence of only one phase having cubic C15 type structure for $x=0.3$ when R=Y, and $x=0.40$ when R=Gd.

Magnetic measurements were performed in the temperature range 4.2–800 K and external fields up to 10 T. The spontaneous magnetizations were determined from magnetization isotherms according to saturation law $M=M_s(1-a/H)+\chi_0 H$. We denoted by χ_0 a field independent susceptibility and a is the coefficient of magnetic hardness. In the paramagnetic range, the magnetic susceptibilities, χ, were determined from their field dependencies, according to the relation $\chi_m=\chi+cM_s/H$, by extrapolation of the

*Corresponding author. Tel.: +40-64-194-315; fax: +40-64-191-906.
E-mail address: burzo@phys.ubbcluj.ro (E. Burzo).

0925-8388/01/$ – see front matter
PII: S0925-8388(01)01046-5

measured values χ_m to $1/H \rightarrow 0$ [7]. By c is denoted a presumed impurity content and M_s is their saturation magnetization. By this method any possible alternation of magnetic susceptibility as result of the presence of small quantities of magnetic ordered phase is avoided. For all compounds the estimated impurity content, if it exists, is smaller than 0.2%.

3. Experimental results

The thermal variations of reciprocal susceptibilities for $YCo_{2-x}Si_x$ compounds are plotted in Fig. 1. At low temperatures, a T^2 dependence was shown for compounds with $x=0$ and 0.1. Since the maxima in susceptibilities for compounds with higher silicon content are shifted to lower temperatures, no reliable temperature dependencies of χ values for samples with $x=0.2$ can be obtained in the temperature range $T<20$ K. Above a characteristic temperature, T^*, the χ *vs.* T curves follow a Curie–Weiss type behavior. The effective cobalt moments decrease when increasing silicon content (Fig. 2). We note that the enhancement factors of susceptibilities when doping with silicon are not as high as previously reported [5].

The thermal variations of spontaneous magnetizations for $GdCo_{2-x}Si_x$ compounds are given in Fig. 3. The Curie temperatures decrease while the saturation magnetizations increase when cobalt is replaced by silicon (Fig. 4). This is in agreement with a ferrimagnetic-type ordering, the gadolinium and cobalt magnetizations being antiparallely oriented.

The reciprocal susceptibilities show downward curvatures as function of temperature and in the high temperature range a linear temperature dependence is shown. According to additional law of susceptibilities we determined the contribution of cobalt atoms to the Curie constant as well as the effective cobalt moments. The M_{eff}(Co) values thus obtained are smaller than those determined in corresponding $YCo_{2-x}Si_x$ compounds (Fig. 2).

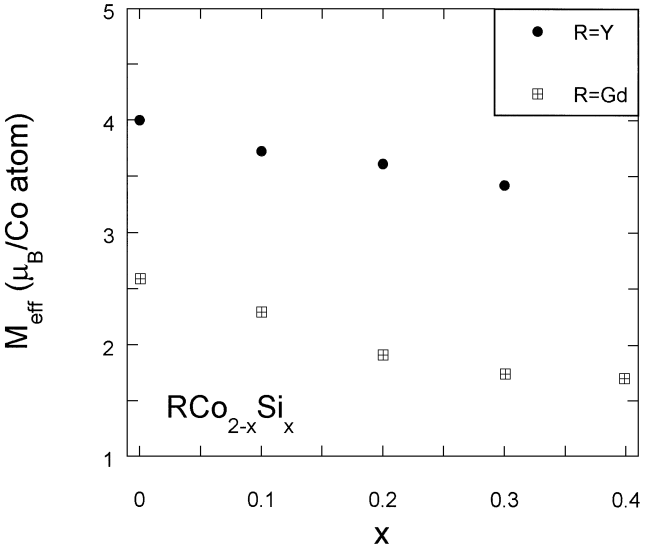

Fig. 2. Compositions dependences of the effective cobalt moments in $RCo_{2-x}Si_x$ (R=Gd, Y) compounds.

4. Band structure calculations

Band structure calculations were carried out by using the ab initio tight binding linear muffin tin orbitals method in the atomic sphere approximation (TB-LMTO-ASA). The detailed procedure of calculations is described elsewhere [8–11]. In the framework of the local density approxi-

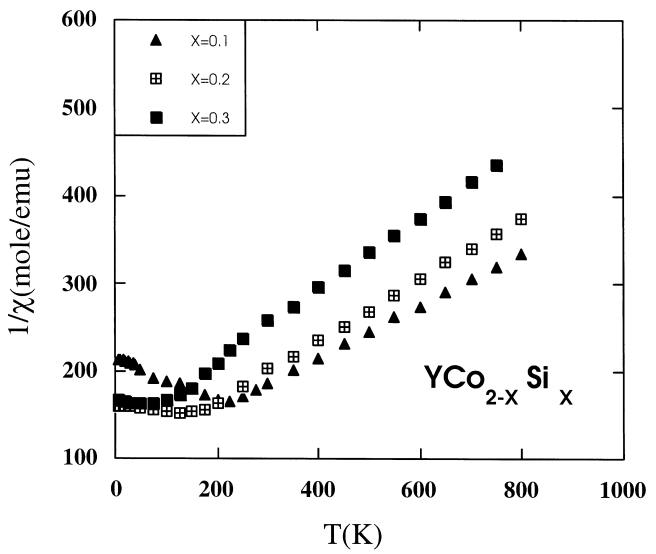

Fig. 1. Thermal variations of reciprocal susceptibilities for $YCo_{2-x}Si_x$ compounds.

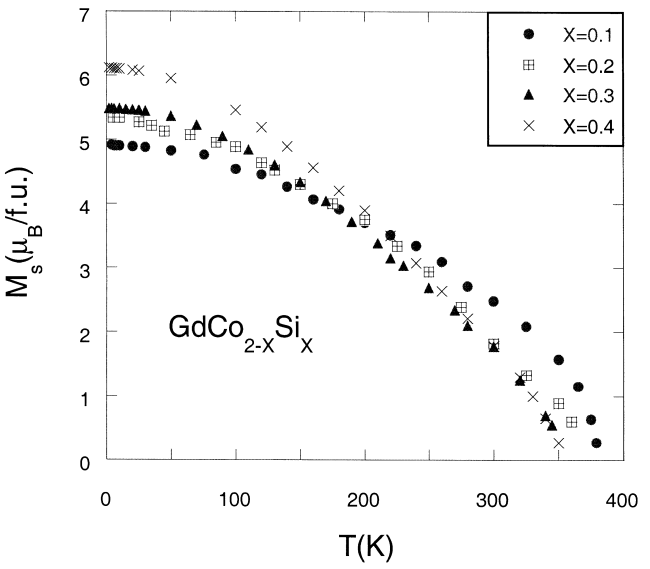

Fig. 3. Thermal variation of spontaneous magnetization for $GdCo_{2-x}Si_x$ system.

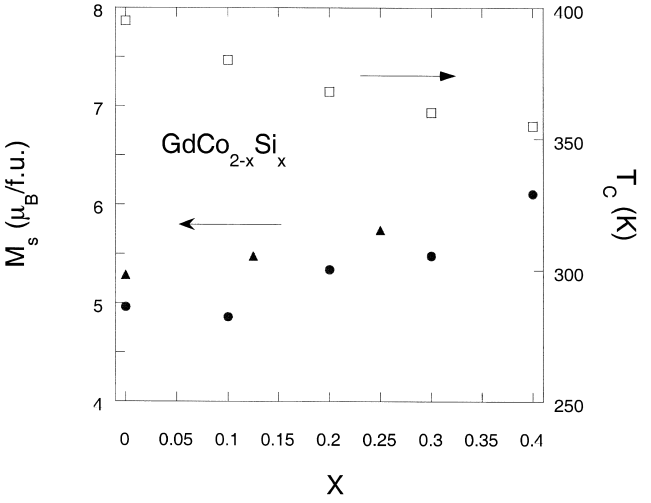

Fig. 4. Composition dependence of the saturation magnetizations at 4.2 K (●) and of Curie temperatures (□). The computed magnetizations determined from band structure calculations are also plotted (▲).

mation (LDA), the total electronic potential is the sum of the external, Coulomb and exchange-correlation potentials [13]. The functional form of the exchange-correlation energy used in the present work was the free-electron gas parameterization of von Barth and Hedin [12]. Relativistic corrections are included without the spin–orbit coupling. An Y_8Co_{16} structure having eight times greater unit cell than that of YCo_2 was assumed. In this cell the cobalt was substituted by one or two silicon atoms, corresponding to compositions $x=0.125$ and $x=0.250$.

The projected total density of states as well as that of Co d band for Y_8Co_{16} is plotted in Fig. 5a. The Fermi level is situated above the characteristic double sharp peak structure of local DOS of cobalt d states. The state densities of Co d and Si p bands for $Y_8Co_{15}Si$ and $Y_8Co_{15}Si_2$ compositions are given in Fig. 5b and c, respectively. The double peak structure of Co d states decrease in intensity, when Si content increases, more important changes being evidenced for the peak situated near Fermi level. The double peak structure is broadened by p–d hybridization and in addition the Co 3d band is shifted to lower energies. The state density at the Fermi level increases slightly for the compound with $x=0.125$ and then decreases. This fact is reflected by the values of computed susceptibilities at 0 K which increase by ~5% for $x=0.125$, being only a little smaller than that of parent compound for $x=0.250$ (Table 1). We mention that the state density at the Fermi level for $YCo_{1.5}Si_{0.5}$ composition outside of the range in which solid solutions are formed, determined by Aoki and Yamada [13], was confirmed by the present study.

The magnetic susceptibilities computed from band structures at 0 K are generally lower than those experimentally determined at 1.7 K. The ratio of measured and calculated values are 1.15 for $x=0$ and increase up to $\cong 3$ for $x=0.25$.

The magnetic moments per formula unit determined from band structure calculation in $GdCo_{2-x}Si_x$ compounds

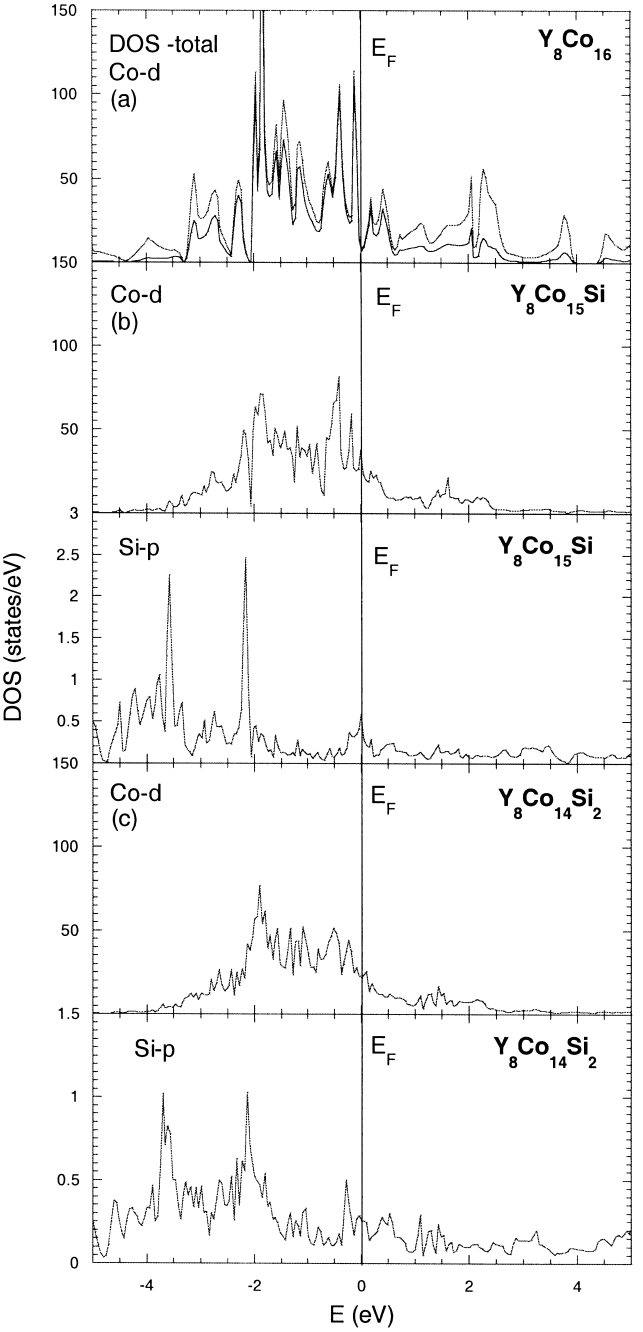

Fig. 5. Projected DOS curves calculated for: (a) Y_8Co_{16} total and Co d; (b) $Y_8Co_{15}Si$, Co d and Si p; and (c) $Y_8Co_{15}Si_2$, Co d and Si p.

show the same trend as those experimentally determined, being greater only by ~0.3 μ_B (5–6%) (Fig. 4).

The gadolinium moments are higher than 7 μ_B due to

Table 1
Magnetic moments of $Gd_8Co_{16-x}Si_x$ at 0 K

Compound	R=Gd (μ_B/atom)			R=Y
	M_{Gd}(4f)	M_{Gd}(5d)	M_{Co}	$\chi\cdot10^3$ (emu/mol)
R_8Co_{16}	7	0.530	−1.12	2.258
$R_8Co_{15}Si$	7	0.493	−0.97	2.571
$R_8Co_{14}Si_2$	7	0.446	−0.77	2.184

polarization of 5d band by 4f electron [14] (Table 1). The polarizations of 5d band decrease slowly when cobalt is replaced by silicon. There is also evidence of the decrease of cobalt moments, which is being confirmed by experimentally determined saturation magnetizations.

5. Discussion

The $YCo_{2-x}Si_x$ compounds show a magnetic behavior similar to that reported for YCo_2 and which can be described by the spin fluctuations model [3,4]. For a nearly ferromagnetic alloy the wave number dependent susceptibility, χ_q, has a large enhancement due to electron–electron interaction for small q values. The temperature dependence of χ_q is significant only for these q values. The average amplitude of local spin fluctuations $\left\langle S_{\text{loc}}^2 \right\rangle = 3k_B T \Sigma_q \chi_q$ is a temperature dependent quantity, increasing until it reaches an upper limit determined by charge neutrality conditions at a temperature T^*. At $T > T^*$ the system behaves as if having local moments. The moments are localized in q-space. For YCo_2 compound if $\left\langle S_{\text{loc}}^2 \right\rangle$ is saturated, the charge neutrality condition leads to an effective moment characteristic for Co^{2+} ion considering only spin contribution [1]. When cobalt is gradually substituted by silicon, there is a p–d type hybridization as evidenced by band structure calculations. The degree of hybridization increases with increasing Si content. This modifies the electronic configuration of cobalt d band and the effective cobalt moments decrease. The calculated susceptibility for YCo_2 compound is close to that experimentally determined. For samples doped with silicon the experimentally determined values are around twice those computed from band structure. The reason for this difference is not clear. In the analysis of experimental data we eliminated the possible influence of magnetic impurities. Probably, the discrepancies may be due to d-d correlation effects which were not considered in computing the density of states.

The effective cobalt moments determined in $GdCo_{2-x}Si_x$ follow the same trend as those obtained in $YCo_{2-x}Si_x$ system although the later are smaller than those obtained in Y-based system. This fact may be attributed to partial quenching of spin fluctuation by internal field [15]. If the exchange field is sufficiently large so that the Zeeman splitting energy of opposite spin states is comparable or larger than the characteristic spin fluctuation energy, the paramagnons no longer have sufficient energy to flip spins and therefore the inelastic spin flip scattering is quenched. A magnetic field of the order of the characteristic spin fluctuation temperature, T_s, is needed to quench the spin fluctuation enhancement [16–18]. A partial quenching of spin fluctuations by external fields was evidenced also in YCo_2 and $LuCo_2$. The decrease of the electronic specific heat constants in a field of 10 T was 4% for YCo_2 and 10% for $LuCo_2$ [18].

The saturation magnetizations per formula unit experimentally determined at 4.2 K for $GdCo_{2-x}Si_x$ system are in good agreement with the computed values (Fig. 4). The polarization of 5d band by 4f electrons decreases slightly from 0.53 μ_B/atom ($x=0$) to 0.446 μ_B for $x=0.250$. The exchange interactions between Gd and Co take place by 5d–3d hybridization which lead to an antiparallel coupling of gadolinium and cobalt magnetizations. The cobalt moments are modified by doping with silicon. These changes may be attributed also to p–d hybridization effects.

Finally, we conclude that the magnetic behavior of cobalt in $YCo_{2-x}Si_x$ and $GdCo_{2-x}Si_x$ may be well described by the theory of spin fluctuations. Temperature induced cobalt moments are evidenced in paramagnetic range. These moments are affected by p–d hybridization as evidenced by band structure calculations and also by partial quenching of spin fluctuations by internal field.

The agreement between the computed magnetizations and those experimentally determined in $GdCo_{2-x}Si_x$ system is rather good. The saturation cobalt moments decrease when increasing silicon content. This leads to the diminution of exchange interactions as evidenced by the lowering of the Curie temperatures.

Acknowledgements

The financial support of CNCSIS is greatly appreciated.

References

[1] E. Burzo, E. Gratz, V. Pop, J. Magn. Magn. Mater. 123 (1993) 159.
[2] M.T. Béal-Monod, Physica B 109–110 (1982) 1837.
[3] T. Moriya, J. Magn. Magn. Mater. 14 (1979) 1.
[4] T. Moriya, J. Magn. Magn. Mater. 100 (1991) 201.
[5] D. Michels, J. Timlin, T. Mihalisin, J. Appl. Phys. 67 (1990) 5289.
[6] N.H. Duc, J. Magn. Magn. Mater. 152 (1996) 219.
[7] L.F. Bates, in: Modern Magnetism, Cambridge University Press, Cambridge, 1951, p. 133.
[8] O.K. Anderson, Phys. Rev. B 12 (1975) 3060.
[9] O.K. Anderson, O. Jepsen, Phys. Rev. Lett. 53 (1984) 2571.
[10] O.K. Anderson, O. Jepsen, D. Glözel, in: F. Bassani, F. Fumi, M.P. Tosi (Eds.), Highlights of Condensed Matter Theory, North Holland, Amsterdam, 1985, p. 59.
[11] R.O. Jones, O. Gunnarson, Rev. Mod. Phys. 61 (1989) 689.
[12] U. von Barth, L. Hedin, J. Phys. C Solid State 5 (1972) 1629.
[13] M. Aoki, H. Yamada, Physica B 177 (1992) 259.
[14] I.A. Campbell, J. Phys. F: Met. Phys. 2 (1972) 147.
[15] E. Burzo, R. Lemaire, Solid State Commun. 84 (1992) 1145.
[16] W.F. Brinkman, S. Engelsberg, Phys. Rev. 169 (1968) 417.
[17] M.T. Béal-Monod, S.K. Ma, D.R. Fredkin, Phys. Rev. Lett. 22 (1968) 928.
[18] K. Ikeda, K.A. Gschneidner, R.J. Stiermann, J.W.E. Tsang, O.D. Mc Masters, Phys. Rev. B 29 (1984) 5039.