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Magnetism and related phenomena in $RE(Co_{1-x}Si_x)_2$ compounds

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Abstract

We report on crystal structure, magnetic, transport and dilatometric studies of the pseudobinary compounds $RE(Co_{1-x}Si_x)_2$ with RE = Nd, Ho and Er for $x \leq 0.15$. The lattice volume of the Ho and Er-based compounds is almost composition invariable, whereas in $Nd(Co_{1-x}Si_x)_2$ for x between 0 and 0.15 it increases by ~ 7%. Already small Si substitutions for Co ($x \leq 0.075$) induce a dramatic increase of T_C both in the Ho and Er compounds without apparent loss of the first order character of the magnetic phase transition, whereas opposite changes of T_C are observed in Nd analogues. These results, together with variations of resistivity and magnetovolume anomalies at T_C and of the Co magnetic moment observed in all three systems is discussed in terms of expected changes of electronic structure and their influence on the hierarchy of exchange interactions and formation of the Co moment in this class of materials. © 1997 Elsevier Science S.A.

Keywords: Rare earth–transition metal compounds; Itinerant electrons; Metamagnetism; Curie temperature; Composition dependent; Magnetovolume effect; Resistivity; Anomalies

1. Introduction

Since the Co 3d-band states in $RECo_2$ (RE = rare-earth element) compounds appear on the verge of magnetism, materials of this type are frequently subjected to intensive experimental and theoretical studies devoted to various aspects of the itinerant electron metamagnetism [1,2]. YCo_2 or $LuCo_2$, which are based on the non-magnetic rare-earth elements, are frequently quoted as typical examples of spin-fluctuation systems with a high characteristic temperature T_{sf}. The Co magnetic moments may be formed and ferromagnetically ordered in a magnetic field which is sufficiently high to induce a metamagnetic transition connected with a sudden splitting of the Co majority and minority 3d sub-bands. The metamagnetic state may be achieved either in external magnetic fields above 60 T or by employing the large exchange field due to ferromagnetically ordered 4f magnetic moments in $RECo_2$ compounds with magnetic rare-earth atoms. This magnetic phase transition at T_C is of the first-order type in the Dy, Ho and Er compounds. When an external magnetic field is applied, the metamagnetic state can be induced at higher temperatures within a limited temperature range above T_C. In $PrCo_2$, $NdCo_2$, $GdCo_2$ and $TbCo_2$, however, the Co atoms bear a stable magnetic moment already at high temperatures and the magnetic ordering transition is of the second-order type.

The fact that the Co 3d states in YCo_2 and $LuCo_2$ are on the brink of magnetism is also documented by the ferromagnetic ground state which can be reached

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by substituting some p-atoms, e.g. Al, for Co [1]. Small Al substitutions in $ErCo_2$, $HoCo_2$, $DyCo_2$ lead to a dramatic increase of T_C. The $RE(Co_{1-x}Al_x)_2$ compounds are the subjects of numerous papers focused on spin-fluctuation [1,3–5] and magnetovolume phenomena [2,6,7]. The effects induced by the Al substitution in the Co sublattice are usually attributed to the lattice expansion due to the larger atomic volume of Al compared to Co [2,3], the decrease of the 3d-electron concentration due to the reduction of Co content, or a strong involvement of Al 3p states in the electron structure (3d–3p hybridization) [8–11].

Effects of the Si substitution for Co were studied by magnetization and resistivity measurements of some $RE(Co_{1-x}Si_x)_2$ compounds [9–13]. Although the lattice volume in $Y(Co_{1-x}Si_x)_2$ and $Lu(Co_{1-x}Si_x)_2$ compounds is altered only slightly with increasing x up to 0.10, we also observe suppression of T_{sf}, a strong enhancement of the susceptibility at low temperatures and the drastic reduction of the critical field for metamagnetism, although ferromagnetism is not reached. The $RE(Co_{1-x}Si_x)_2$ compounds with RE = Gd, Tb, Dy and Er have been studied so far [11,14]. In this paper we compare effects of Si doping in the Nd, Ho and Er based materials to demonstrate analogies and differences in the physics of the light and heavy rare-earth $RECo_2$ compounds.

2. Experimental

The $RE(Co_{1-x}Si_x)_2$ samples (RE = Nd, Ho and Er) for $x \leq 0.15$ were synthesised by melting stoichiometric mixtures of components (minimum purity of 3N5) under argon atmosphere. The melted buttons were wrapped in Ta foil, sealed under argon in silica tubes and annealed at 950°C for 50 h. The X-ray diffraction analysis revealed only the expected cubic C15 phase. The observed values of the lattice parameter a are shown in Table 1. We can see that whereas the volume of the Ho and Er compounds is nearly composition invariable, an increase of approx. 7% is observed in $Nd(Co_{1-x}Si_x)_2$ for x between 0 and 0.15.

Table 1
Lattice parameter a of $Nd(Co_{1-x}Si_x)_2$, $Ho(Co_{1-x}Si_x)_2$ and $Er(Co_{1-x}Si_x)_2$ compounds

	$Nd(Co_{1-x}Si_x)_2$	$Ho(Co_{1-x}Si_x)_2$	$Er(Co_{1-x}Si_x)_2$
x	a [pm]	a [pm]	a [pm]
0	728.2	716.6	714.8
0.025	—	—	715.5
0.05	—	716.2	—
0.075	735.2	716.2	715.9
0.10	742.9	—	716.3
0.15	745.0	717.8	716.2

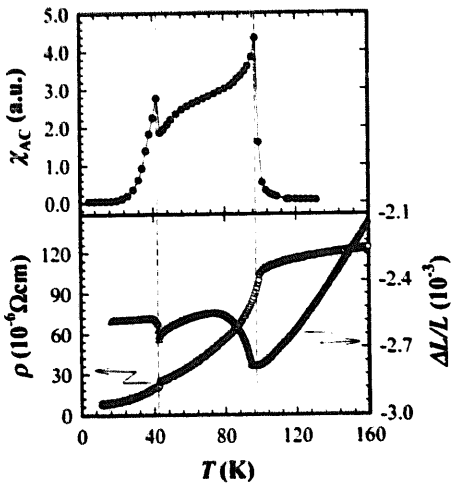

Fig. 1. Temperature dependence of the real part of the AC susceptibility (●), electrical resistivity (○) and thermal expansion (Δ) in $NdCo_2$.

The magnetization was measured in a Quantum Design SQUID magnetometer in fields up to 5 T and in some cases by the induction method in fields up to 10 T. The resistivity and the magnetoresistance (in the fields up to 9 T) were measured on bar-shaped samples (size ~ $1 \times 1 \times 7$ mm^3) using the AC four-terminal measuring technique. The thermal expansion was measured using micro-strain gauges (Micro-Measurements, SK-350). The AC susceptibility was recorded at a frequency of 90 Hz using a SR 530 lock-in amplifier.

3. Results and discussion

In Figs. 1–3 we can see the AC susceptibility, electrical resistivity and thermal expansion behaviour of $NdCo_2$, $HoCo_2$ and $ErCo_2$. The first-order magnetic phase transition to magnetic ordering at T_C in the latter two compounds is reflected in a step-like jump in the magnetization, a sharp peak in the AC susceptibility, a resistivity drop $\Delta\rho$ and an abrupt expansion of the lattice, whereas usual 'second-order-type' resistivity and thermal-expansion anomalies (yielding just a discontinuity of the derivative at T_C) are exhibited by $NdCo_2$. The additional susceptibility and expansion anomaly at $T_R \ll T_C$ observed in $NdCo_2$ and $HoCo_2$ is the effect attributed to the reorientation of the easy-magnetization axis in these materials [15,16].

Closer inspection of the magnetization and magnetoresistance isotherms at temperatures above T_C helps us to emphasise differences of magnetism in the light and heavy rare-earth $RECo_2$ compounds. The results obtained for $ErCo_2$, which are displayed in Figs. 4

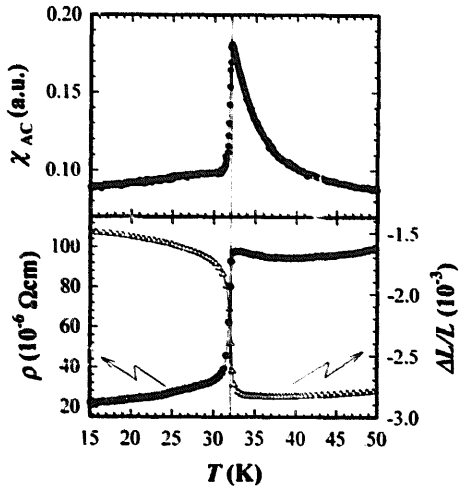

Fig. 2. Temperature dependence of the real part of the AC susceptibility (●), electrical resistivity (○) and thermal expansion (Δ) in $ErCo_2$.

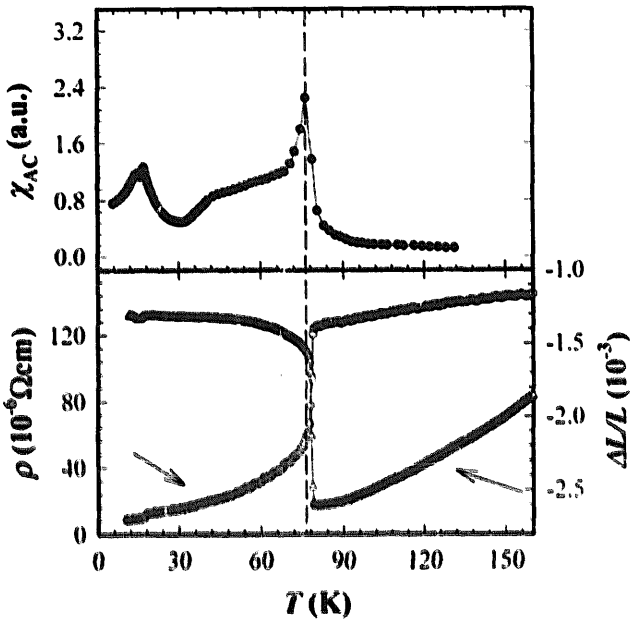

Fig. 3. Temperature dependence of the real part of the AC susceptibility (●), electrical resistivity (○) and thermal expansion (Δ) in $HoCo_2$.

and 5, are in a good agreement with previous reports [4,12] as concerns the metamagnetic behaviour in a limited temperature range above T_C (T_C = 33 K in $ErCo_2$). The critical field (B_C) of the metamagnetic transition increases with increasing temperature, whereas the magnetization step (ΔM) at the metamagnetic transition diminishes gradually and vanishes above 48 K. Magnetoresistance data demonstrate that the metamagnetic transition is accompanied by a considerable drop of the resistivity. The magnetoresistance value above the metamagnetic transition observed at 34 K (just above T_C) roughly scales with the negative step (~ −60%) observed in zero magnetic field for the temperature dependence of the resistivity below T_C. In the case of $HoCo_2$ (T_C = 77 K) we have observed analogous behaviour, which is in agreement with literature reports [12]. On the other hand, no metamagnetism can be traced in magnetization curves of $NdCo_2$ above T_C (= 98 K) shown in Fig. 6.

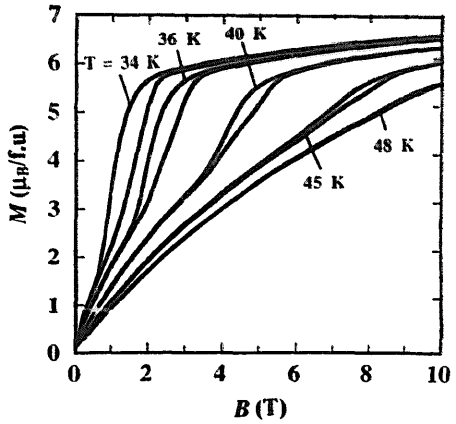

Fig. 4. Magnetization isotherms of $ErCo_2$ at temperatures above T_C.

The resistivity behaviour of the heavy rare-earth $RECo_2$ compounds in the critical region around T_C is usually explained within the following scenario. The resistivity above T_C is mainly affected by a spin-disorder scattering on paramagnetic rare-earth moments and by electron spin-fluctuation scattering depending on the dynamics of spin fluctuations in the Co 3d-band [17]. When lowering the temperature, the 4f-moments which order ferromagnetically at T_C produce strong uniform exchange interactions acting on the Co 3d states. When this action is sufficient to split the 3d majority and minority sub-bands, the spin fluctuations at the Co-sites are quenched and the 3d-band metamagnetic state is induced by a first order transition. Consequently, the scattering is drastically suppressed, which yields the resistivity drop. The obvious effect of a dramatic reconstruction of the Fermi surface on transport properties at the metamagnetic transition should be considered as well. The abrupt lattice expansion observed in zero field at T_C (Figs. 2 and 3) or at metamagnetic transition induced at temperatures above T_C can be naturally attributed to the positive magnetovolume effect accompanying formation of the Co magnetic moment, and this effect allows a detailed monitoring of the Co-moment formation in different conditions. Similar phenomena accompanying the Co 3d itinerant electron metamagnetism are obviously absent in $NdCo_2$ where the Co moment exists already in the paramagnetic range.

As can be seen in Fig. 7, Si substitutions in the Co sublattice have a strikingly different impact on T_C in

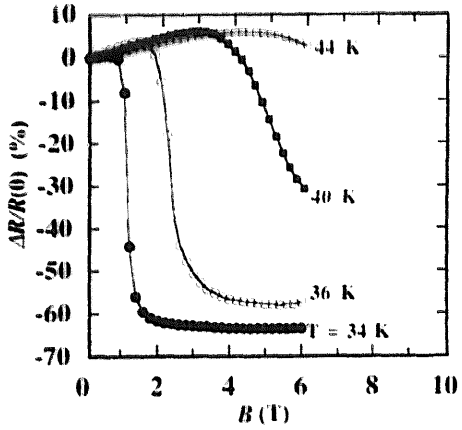

Fig. 5. Magnetoresistance curves of $ErCo_2$ ($\Delta R/R(0) = [R(B) - R(0)]/R(0)$ vs. B plots in decreasing magnetic field, where $R(0)$ and $R(B)$ are the resistance in zero and applied magnetic fields) measured at temperatures above T_C.

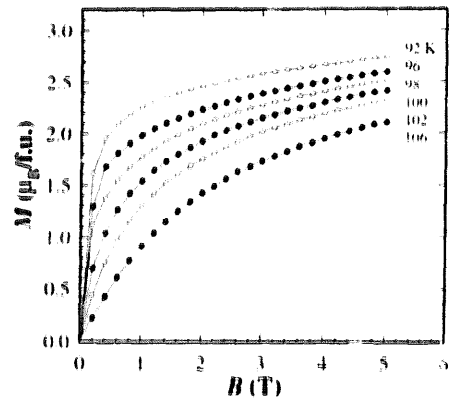

Fig. 6. Magnetization isotherms of $NdCo_2$ at temperatures around T_C.

the light rare-earth $RE(Co_{1-x}Si_x)_2$ compounds represented by the $Nd(Co_{1-x}Si_x)_2$ system and in the heavy rare-earth ones as demonstrated by the Ho and Er analogues. Whereas T_C of $Nd(Co_{1-x}Si_x)_2$ compounds decreases with increasing x which one would expect as a natural result when diluting a 'magnetic' element (Co) by a 'non-magnetic' one (Si), a rapid increase of the ordering temperature is observed in Ho and Er counterparts (for x up to 0.075 and 0.1, respectively). For Si content increasing beyond $x = 0.075$ a maximum of T_C in the latter two systems is reached and followed finally by a decreasing trend. Then the magnetization anomaly associated with magnetic ordering becomes progressively broadened indicating loss of the first-order character of the magnetic phase transition, which may reflect both the disappearance of the Co metamagnetism and the effects of the increasing substitutional disorder in the Co sublattice. The spin-reorientation temperature T_R is, however, continuously lowered with increasing Si concentration both in the Nd and Ho systems.

The temperature dependence of the electrical resistivity of some typical $Ho(Co_{1-x}Si_x)_2$ compounds is

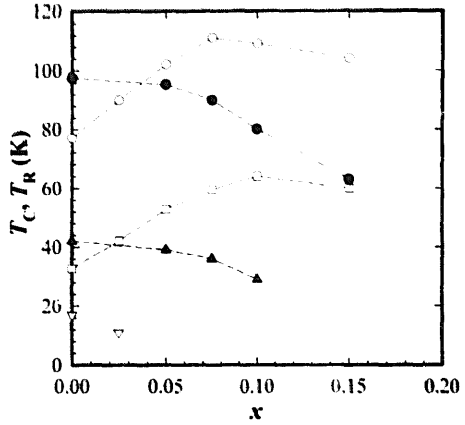

Fig. 7. Concentration dependence of T_C and T_R in $RE(Co_{1-x}Si_x)_2$ for RE = Nd (● and ▲), Ho (○ and △) and Er (□).

presented in Fig. 8. The first order transition to magnetic ordering in compounds with $x \leq 0.075$ is manifest in a sudden drop of the resistivity $\Delta\rho$, which is gradually reduced with increasing Si content and vanishes for x beyond 0.075. In compounds with $x \leq 0.05$, the resistivity decreases monotonously with further lowering temperature and tends to saturate in the low-temperature limit. The resistivity drop $\Delta\rho$ in $Ho(Co_{0.925}Si_{0.075})_2$ at T_C is considerably reduced, the low-temperature behaviour is modified and the resistivity increases with decreasing temperature. This effect becomes progressively pronounced upon further increasing Si content. Similar development of resistivity behaviour also has been reported for some other pseudobinary series, e.g. the $Ho(Co_{1-x}Al_x)_2$ compounds [17]. When considering possible sources of the resistivity behaviour we should emphasise that for the Er system we observe an analogous concentration evolution of the electrical resistivity. The resistivity behaviour of $Nd(Co_{1-x}Si_x)_2$ compounds is, however, considerably different, as can be seen in Fig. 9. The second order type transition in $NdCo_2$ is reflected by a sudden change of slope of the ρ vs. T curve at T_C (no discontinuity at T_C). Nevertheless, the overall reduction of the resistivity between T_C and the low temperature limit is comparable [$\rho(T_C) - \rho_{LT} \sim 100$ $\mu\Omega$cm] in all three $RECo_2$ compounds studied. The value of $\rho(T_C) - \rho_{LT}$ (see Fig. 10) in the $Ho(Co_{1-x}Si_x)_2$ compounds (and their Er counterparts) decreases with Si doping faster than in the $Nd(Co_{1-x}Si_x)_2$ system for two reasons: (a) $\Delta\rho$ (drop below T_C) is diminished rapidly and (b) a contribution which increases with decreasing temperature develops. The latter takes over for $x \geq 0.075$ and the value of $\rho(T_C) - \rho_{LT}$ becomes negative. This contribution is evidently absent in the Nd system, where the $\rho(T)$ curve flattens (mainly below T_C) with the Si substitution partly due to the decreasing Co moment (discussed lower) and partly due the additional conduction electron scattering caused by the increasing in-

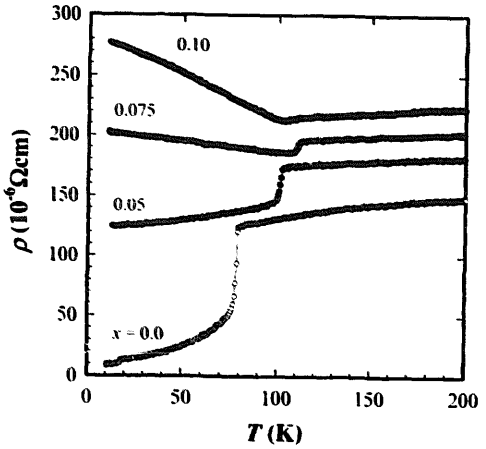

Fig. 8. Temperature dependence of the electrical resistivity of $Ho(Co_{1-x}Si_x)_2$ compounds for $x = 0$, 0.05, 0.075 and 0.1.

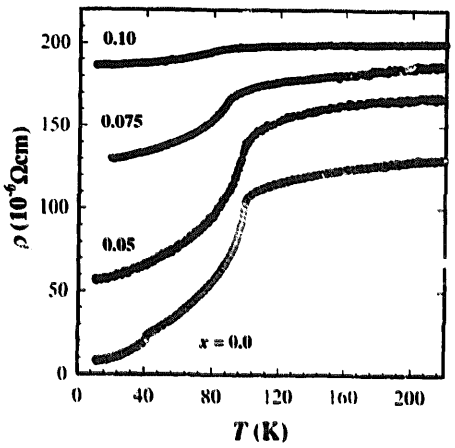

Fig. 9. Temperature dependence of the electrical resistivity of $Nd(Co_{1-x}Si_x)_2$ compounds for $x = 0$, 0.05, 0.075 and 0.1.

coherence of the crystal lattice (also incoherent canting of magnetic moments due to locally frustrated interactions). These phenomena must also be present in the heavy $RE(Co_{1-x}Si_x)_2$ compounds. Besides that, however, a mechanism responsible for the low-temperature upturns in the ρ vs. T dependencies should exist. Possible involvement of spin fluctuations preserved locally to low temperatures in conditions of inhomogeneities in the Co sublattice due to the Si doping may be speculated upon. Experiments which may review the dynamics of such fluctuations are desirable to resolve this problem.

In Figs. 11 and 12 the evolution of thermal expansion in $Nd(Co_{1-x}Si_x)_2$ and $Ho(Co_{1-x}Si_x)_2$ compounds is presented. After an initial increase by approx. 10% for $x \leq 0.025$ in the latter system, the magnetovolume effect ω_s [and the deduced Co moment μ_{Co} (shown in Fig. 13): $\omega_s = k\mu_{Co}^2$, k is the magnetoelastic coupling constant] decreases upon further increasing x. Moreover, for x between 0.075 and 0.1, a clear change of type of the magnetic phase transition at T_C is observed (the volume step $\Delta V/V = 3\,\Delta L/L$ at T_C vanishes). Nevertheless, the value of ω_s in $Ho(Co_{0.9}Si_{0.1})_2$ points to a Co moment of approximately 0.9 μ_B (for further Si doping the Co moment is reduced) which, however, is not a result of any metamagnetism at T_C but may be considered as a stable Co magnetic moment similar to the light rare-earth $RECo_2$ (including $GdCo_2$ and $TbCo_2$) compounds. Neutron scattering or some other relevant microscopic experiments, however, are expected to confirm this conjecture.

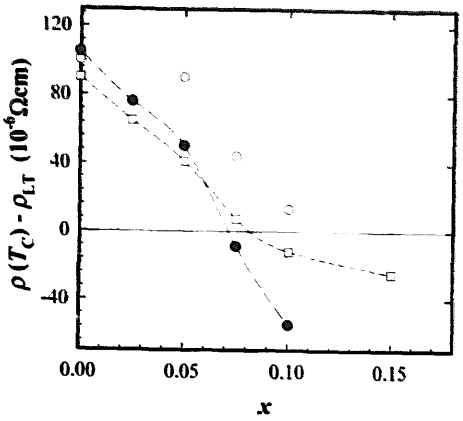

Fig. 10. Concentration dependence of $\rho(T_C) - \rho_{LT}$ in $RE(Co_{1-x}Si_x)_2$ for RE = Nd (○), Ho (●) and Er (□).

The results document that the role of the Si substitution in the $RECo_2$ compounds does not consist of a simple dilution of the Co sublattice, but besides the effective reduction of overlap integral of 3d wavefunctions between Co–Co nearest neighbours (which may lead to a narrowing of the Co 3d band) and the variation of the count of Co 3d electrons in the system, a considerable involvement of the Si 3p states in the electronic structure of the system has to be considered, namely their hybridization with the Co 3d states and the RE 5d states.

The leading component of the exchange interaction coupling the RE magnetic moments and determining the ordering temperature in the heavy rare-earth $RECo_2$ materials without stable Co moments ($DyCo_2$, $HoCo_2$, $ErCo_2$, $TmCo_2$) is born from the hybridization of the RE 5d-electron states with the Co 3d states. The strong enhancement of the exchange interaction deduced from the increasing T_C in the heavy-rare earth systems can be tentatively attributed to an additional contribution to the exchange interaction which arises from the 5d–3p (Si) hybridization. In $NdCo_2$ and the other $RECo_2$ compounds with a stable Co magnetic moment the direct Co–Co (3d–3d) exchange interaction also contributes substantially, acting as a leading term and yields considerably larger T_C values. Since the Co moment is instantly reduced with increasing Si content in the $Nd(Co_{1-x}Si_x)_2$ compounds, the Co–Co exchange interaction weakens

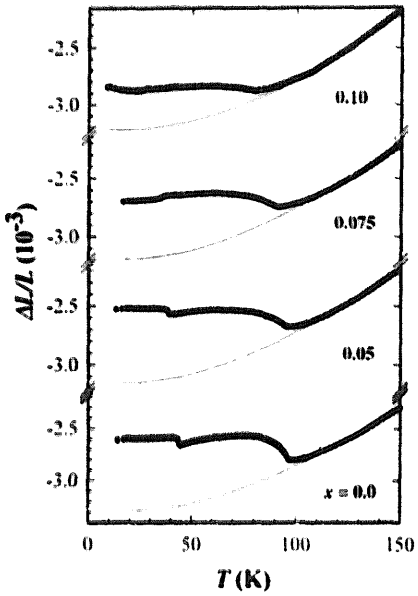

Fig. 11. Temperature dependence of the thermal expansion of $Nd(Co_{1-x}Si_x)_2$ compounds for $x = 0$, 0.05, 0.075 and 0.1.

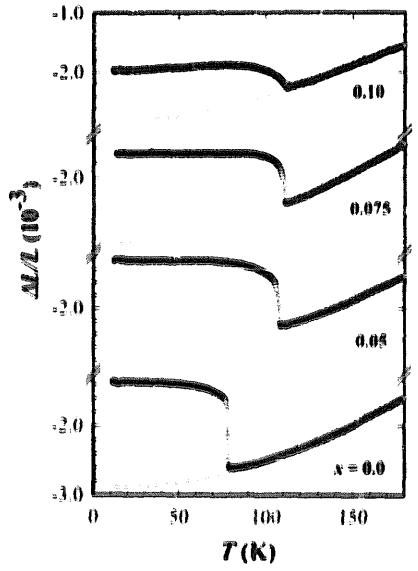

Fig. 12. Temperature dependence of the thermal expansion of $Ho(Co_{1-x}Si_x)_2$ compounds for $x = 0$, 0.05, 0.075 and 0.1.

reducing T_C as a direct consequence. The effects of the 3d(Co)–3p(Si) hybridization involving both the variation of Co moments and exchange interaction within the Co sublattice cannot be omitted.

Acknowledgements

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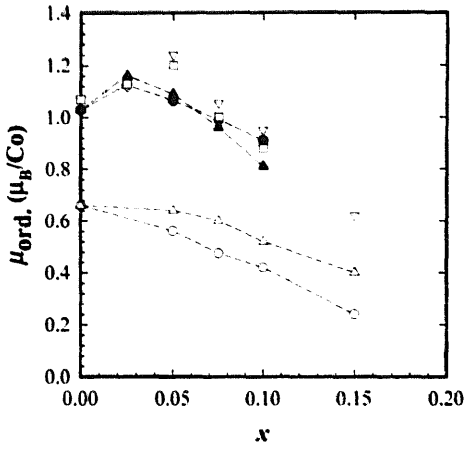

Fig. 13. Concentration dependence of the Co ordered magnetic in $RE(Co_{1-x}Si_x)_2$ for RE = Nd (○ and △), Ho (● and ▲) and Er (□ and ▽) deduced from the saturated magnetization M_s (obtained by fitting the low-temperature magnetization data by the law of approach to saturation and supposing $\mu_{Nd} = 2.3\ \mu_B$ parallel to μ_{Co}, and $\mu_{Ho} = 10\ \mu_B$ and $\mu_{Er} = 9\ \mu_B$ antiparallel to μ_{Co}) and from the magnetovolume effect ω_s, respectively.

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