Co MAGNETISM AND MAGNETOVOLUME PHENOMENA IN $RE(Co_{1-x}Si_x)_2$ COMPOUNDS

TRAN DINH CUONG, LADISLAV HAVELA, VLADIMÍR SECHOVSKÝ,
ZDENĚK ARNOLD, JIŘÍ KAMARÁD

Results of magnetic and dilatometric studies of the $RE(Co_{1-x}Si_x)_2$ compounds with RE = Nd, Ho and Er for $x \leq 0.15$ are presented. The lattice cell volume of the Ho and Er compounds is invariable with respect to x, whereas the $Nd(Co_{1-x}Si_x)_2$ lattice expands by $\cong 7\%$ when x increases up to 0.15. Si substitutions for Co ($x \leq 0.075$) induce a dramatic increase of Curie temperature (T_C) both in the Ho and Er compounds. Slight reduction of T_C is observed in Nd analogues. Co magnetism in these materials is reflected in pronounced magnetovolume phenomena below T_C. Results are discussed in terms of expected changes of electronic structure and their influence on the hierarchy of exchange interactions and formation of the Co moment.

MAGNETISMUS Co A MAGNETOOBJEMOVÉ JEVY VE SLOUČENINÁCH $RE(Co_{1-x}Si_x)_2$

Jsou prezentovány výsledky magnetických a dilatometrických studií sloučenin $RE(Co_{1-x}Si_x)_2$, kde RE = Nd, Ho a Er pro $x \leq 0{,}15$. Zatímco mříž $Nd(Co_{1-x}Si_x)_2$ expanduje o $\cong 7$ % se vzrůstem x na 0,15, mřížový objem sloučenin s Ho a Er nezávisí na x. Substituce Si za Co ($x \leq 0{,}075$) indukuje dramatický vzrůst Curieovy teploty (T_C) jak v holmiových, tak i v erbiových sloučeninách, kdežto slabá redukce T_C je pozorována u Nd analogů. Kobaltový magnetismus v těchto materiálech je reflektován ve výrazných magnetoobjemových jevech pod T_C. Výsledky jsou diskutovány vzhledem k očekávaným změnám elektronové struktury a vlivu těchto změn na hierarchii výměnných interakcí a formování kobaltového momentu.

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

Ing. T. D. Cuong, RNDr. L. Havela, CSc., Prof. RNDr. V. Sechovský, DrSc., Department of Metal Physics, Charles University, Ke Karlovu 5, CZ-121 16 Praha 2, Czech Republic, phone & fax: +420 2 21911351, e-mail: {cuong,havela,sech}@mag.mff.cuni.cz

RNDr. Z. Arnold, CSc., Ing. J. Kamarád, CSc., Institute of Physics, Academy of Sciences of the Czech Republic, Cukrovarnická 10, CZ-162 00 Praha 6, Czech Republic, phone: +420 2 24311137, fax: +420 2 3123184, e-mail: {arnold,kamarad}@fzu.cz

subjected to intensive experimental and theoretical studies devoted to various aspects of the itinerant electron metamagnetism [1–3]. YCo_2 or $LuCo_2$, with non-magnetic elements on the rare-earth positions, 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 magnetic field which is sufficiently high to induce a metamagnetic transition based on 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 a large exchange field due to ferromagnetically ordered 4f magnetic moments in $RECo_2$ compounds with RE = Dy, Ho and Er. In the latter-type compounds this happens just at Curie temperature (T_C) when the RE magnetic moments order ferromagnetically and the magnetic phase transition is then of the first-order type. Magnetic moments in the Co sublattice are ordered ferromagnetically and are antiparallel to the RE moments. The metamagnetic state can be induced also at temperatures somewhat above (T_C) when the exchange field is assisted by an external magnetic field [4]. The metamagnetic transitions connected with formation and ordering of the Co moments are accompanied by sharp anomalies in transport and magnetovolume properties [5]. 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 phase transition at T_C, where both the Co and RE magnetic moments order ferromagnetically, 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 by substituting some p-atoms, e.g. Al, for Co [2]. Small Al substitutions in $ErCo_2$, $HoCo_2$, $DyCo_2$ lead to a dramatic increase of T_C. The $RE(Co_{1-x}Si_x)_2$ compounds are subjects of numerous papers focused on spin-fluctuation [2, 6–8] and magnetovolume phenomena [3, 9, 10]. 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 [3, 5], 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) [11–14].

Effects of the Si substitution for Co were studied by magnetization and resistivity measurements of some $RE(Co_{1-x}Si_x)_2$ compounds [12–15]. 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 [14, 16]. This paper is focused on effects of Si doping on Co magnetism and related magnetovolume phenomena 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 $RE(Co_{1-x}Si_x)_2$ polycrystalline samples (RE = Nd, Ho and Er) for $x \leq$ ≤ 0.15 were synthesized 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 hours. The X-ray diffraction analysis revealed only the expected cubic $MgCu_2$-type structure of parent compounds. The observed values of the lattice parameter a are shown in Table 1. We can see that the volume of the Ho and Er compounds is nearly composition invariable with respect to x whereas a lattice expansion of about 7% is observed in $Nd(Co_{1-x}Si_x)_2$ for x increasing between 0 and 0.15.

T a b l e 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

x	$Nd(Co_{1-x}Si_x)_2$ a [nm]	$Ho(Co_{1-x}Si_x)_2$ a [nm]	$Er(Co_{1-x}Si_x)_2$ a [nm]
0	0.7282	0.7166	0.7148
0.05	–	0.7162	0.7155
0.075	0.7352	0.7162	0.7159
0.10	0.7429	–	0.7163
0.15	0.7450	0.7178	0.7162

The magnetization was measured in a Quantum Design SQUID magnetometer in fields up to 5 T. The compressibility and the thermal expansion were measured using micro-strain gauges (Micro-Measurements Inc., SK-350) fixed on a plane sample surface. The strain gauges were calibrated using the relevant reference data of compressibility and thermal expansion of silica, Cu, and Fe. The pressure experiments were performed in a CuBe cell with fixed hydrostatic pressure up to 0.9 GPa cooled in the He closed-cycle refrigerator. The pressure was measured *in situ* using a manganin pressure sensor.

3. Results and discussion

In Figs. 1–3 we can see the thermal expansion behaviour of selected $Ho(Co_{1-x}Si_x)_2$, $Er(Co_{1-x}Si_x)_2$ and $Nd(Co_{1-x}Si_x)_2$ compounds, respectively. The first-order magnetic phase transition to magnetic ordering at T_C in $HoCo_2$ or $ErCo_2$ is reflected in an abrupt expansion of the lattice, whereas an usual "second-order-

-type" thermal-expansion anomaly (yielding just a discontinuity of the derivative at T_C) is exhibited by NdCo$_2$. The additional susceptibility and expansion anomalies at $T_R \ll T_C$ observed in NdCo$_2$ and HoCo$_2$ are the effect attributed to the reorientation of the easy-magnetization axis [17, 18]. The abrupt lattice expansion observed in zero field at T_C (Figs. 1 and 2) is attributed to the positive magneto-volume effect accompanying sudden formation of the Co magnetic moment. Such effect is obviously absent in NdCo$_2$ where the Co moment exists already in the paramagnetic range.
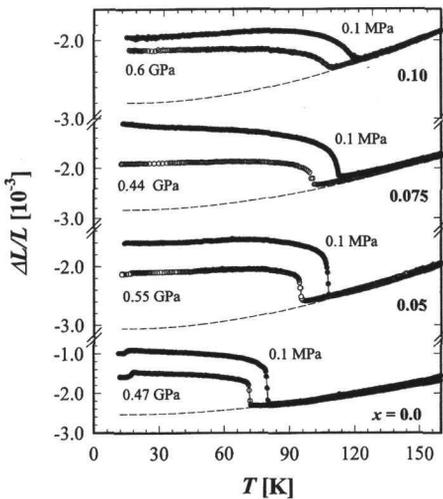

Fig. 1. Temperature dependence of the thermal expansion of Ho(Co$_{1-x}$Si$_x$)$_2$ compounds for $x = 0$ (in 0.1 MPa and 0.47 GPa), 0.05 (in 0.1 MPa and 0.55 GPa), 0.075 (in 0.1 MPa and 0.44 GPa), and 0.1 (in 0.1 MPa and 0.6 GPa).
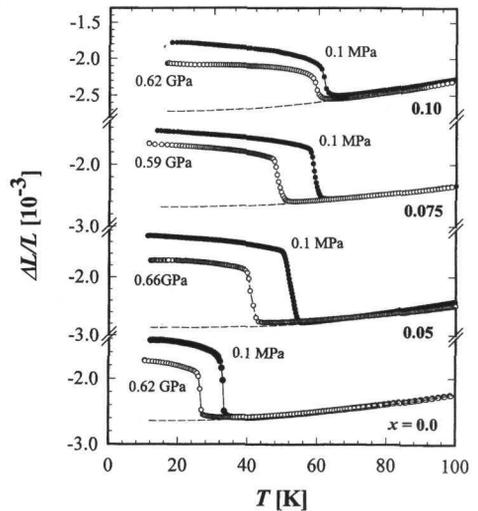
Fig. 2. Temperature dependence of the thermal expansion of Er(Co$_{1-x}$Si$_x$)$_2$ compounds for $x = 0$ (in 0.1 MPa and in 0.62 GPa), 0.05 (in 0.1 MPa and 0.66 GPa), 0.075 (in 0.1 MPa and 0.59 GPa), and 0.1 (in 0.1 MPa and 0.62 GPa).

Further, one can see that Si substitutions for Co have a strikingly different impact on T_C in 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 (for review see also Fig. 4). Whereas T_C of Nd(Co$_{1-x}$Si$_x$)$_2$ compounds becomes only slightly reduced 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. However, the spin-reorientation temperature T_R is gradually lowered with increasing Si concentration both in the Nd and Ho systems. The first order transition to magnetic ordering in Ho and Er compounds with $x \leq 0.075$ and 0.1, respectively, is manifested by a sudden lattice expansion which is gradually reduced with increasing Si content and vanishes for x beyond the mentioned concentrations. Then the volume 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.

Magnetovolume data for $Y(Co_{1-x} Al_x)_2$ [19] allow an assumption that the Co sub-lattice plays the dominant role in the magnetovolume phenomena in $RECo_2$ compounds. Then, we may esti-
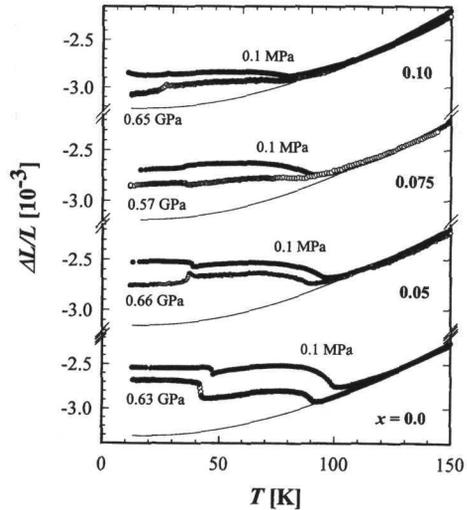

Fig. 3. Temperature dependence of the thermal expansion of $Nd(Co_{1-x}Si_x)_2$ compounds for $x = 0$ (in 0.1 MPa and in 0.63 GPa), 0.05 (in 0.1 MPa and in 0.66 GPa), 0.075 (in 0.1 MPa and in 0.57 GPa), and 0.1 (in 0.1 MPa and in 0.65 GPa).
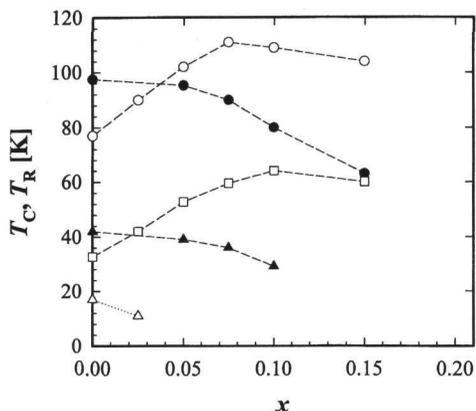
mate the Co moment in our systems (see Fig. 5) from the formula $\omega_s \cong C\mu_{Co}^2$ (C is the magnetoelastic coupling constant). Ho (Er) compounds show an initial increase of μ_{Co} by approximately 10 (20)% for $x \leq 0.025$ (0.05) followed by a monotonous decrease for further increasing x. The abrupt lattice expansion $\Delta V/V = 3\Delta L/L$ at T_C also vanishes for $x > 0.075$ (0.1) where the Co metamagnetism disappears. The value of ω_s in both the Ho and Er systems at higher Si concentrations point to a considerable residual Co moment which, however, is not a result of any metamagnetism at T_C but may be tentatively attributed to a stable Co moment similar to $NdCo_2$. However, neutron scattering or some other relevant microscopic experiments are expected to confirm this conjecture.

In Figs. 1–3 one can also see that application of external pressure reduces T_C in all three systems (Nd, Ho and Er compounds) with almost composition invariant (for $x \leq 0.075$) values of $\partial \ln T_C/\partial p \cong -0.15$, -0.23, and -0.30 GPa^{-1}, respectively, pointing to the linearly extrapolated critical pressures for disappearance of ferromagnetism $p_c \cong 6.7$, 4.3, and 3.3 GPa, respectively. The compressibility of the $Ho(Co_{1-x}Si_x)_2$ and $Er(Co_{1-x}Si_x)_2$ compounds which is $\kappa_p \cong 9.8 \times 10^{-3}$ GPa^{-1}

Fig. 4. Concentration dependence of T_C and T_R in $RE(Co_{1-x}Si_x)_2$ for RE = Nd (● and ▲), Ho (○ and △) and Er (□).
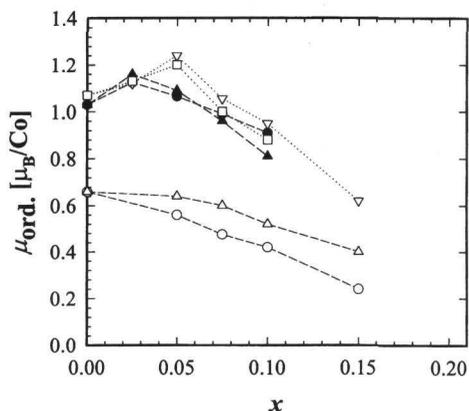
Fig. 5. Concentration dependence of the Co ordered magnetic in $RE(Co_{1-x}Si_x)_2$ for RE = Nd (○ and △), Ho (● and ▲), and Er (□ and ▽) deduced from the saturated magnetization M_s (obtained by fitting the low-temperature magnetization date by the law of approach to saturation and supposing $\mu_{Nd} = 2.3\,\mu_B$ 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.

and 8.9×10^{-3} GPa^{-1} at room temperature increases drastically below T_C, where $\kappa_f = \kappa_p + \Delta\kappa$ with $\Delta\kappa = 1.1 \times 10^{-3}$ GPa^{-1} and 1.4×10^{-3} GPa^{-1} for ErCo$_2$ and HoCo$_2$, respectively. This softening is intimately connected with the reduction of the spontaneous magnetostriction due to pressure-induced suppression of the Co moment.

A rough estimation of the relevant softening of compressibility in the Nd(Co$_{1-x}$Si$_x$)$_2$ compounds gives a value $\Delta\kappa = \omega_s/p_c \cong 2 \times 10^{-4}$ GPa^{-1} which is smaller by one order of magnitude in comparison with the Ho and Er compounds and well comparable with very small magnetostriction of all the ferromagnetic Co-rich alloys (including the amorphous Co-based alloys).

The obtained 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 wave-functions 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 yielding 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 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.

REFERENCES

[1] WOHLFARTH, E. P.—RHODES, P.: Phil. Mag., *7*, 1962, p. 1917.
[2] GOTO, T.—ARUGA KATORI, H.—SAKAKIBARA, T.—MITAMURA, H.—FUKAMICHI, K.—MURATA, K.: J. Appl. Phys., *76*, 1994, p. 6682 and references therein.
[3] DUC, H. N.—HIEN, T. D.—BROMMER, P. E.—FRANSE, J. J. M.: J. Magn. Magn. Mater., *104–107*, 1992, p. 1252 and references therein.
[4] FRANSE, J. J. M.—RADVANSKI, R.: In: Handbook of Magnetic Materials. Vol. 7. Ed.: Buschow, K. H. J. Amsterdam, North-Holland 1993, p. 307.
[5] FOURNIER, J. M.—GRATZ, E.: In: Handbook on the Physics and Chemistry of Rare Earths. Vol. 17. Ed.: Gschneidner, K. A., Jr., Eyring, L., Choppin, G. R., Lander, G. H. Amsterdam, North-Holland 1993, p. 409 and references therein.
[6] PILLMAYR, N.—HILSCHER, G.—FORSHUBER, M.—YOSHIMURA, K.: J. Magn. Magn. Mater., *90–91*, 1990, p. 964.
[7] DUC, N. H.: J. Magn. Magn. Mater., *131*, 1994, p. 224.
[8] DUC, N. H.—BROMMER, P. E.—LI, X.—DE BOER, F. R.—FRANSE, J. J. M.: Physica B, *212*, 1995, p. 83.
[9] ARMITAGE, J. G. M.—GRAHAM, R. G.—RIEDI, P. C.—ABELL, J. S.: J. Phys.: Condens. Matter., *2*, 1990, p. 8779.
[10] DUC, N. H.—VOIRON, J.—HOLTMEIER, S.—HAEN, P.—LI, X.: J. Magn. Magn. Mater., *125*, 1993, p. 323.
[11] DUBENKO, I. S.—LEVITIN, R. Z.—MARKOSYAN, A. S.— SILANT'EV, V. I.—SNEGIREV, V. V.: J. Magn. Magn. Mater., *94*, 1991, p. 287.
[12] AOKI, M.—YAMADA, H.: Physica B, *177*, 1992, p. 259.
[13] MURATA, K.—FUKAMICHI, K.—GOTO, T.—SUZUKI, K. —SAKAKIBARA, T.: J. Phys.: Condens. Matter., *2*, 1994, p. 6659.

[14] DUC, N. H.: J. Magn. Magn. Mater., *152*, 1996, p. 219.

[15] MICHELS, D.—TIMLIN, J.—MIHALISHIN, T.: J. Appl. Phys., *67*, 1990, p. 5289.

[16] CUONG, T. D.—HAVELA, L.—SECHOVSKÝ, V.—ANDREEV, A. V.—ARNOLD, Z.—KAMARÁD, J.—DUC, N. H.: J. Appl. Phys., *81*, 1997, p. 4221.

[17] STEINER, W.—GRATZ, E.—ORTBAUER, H.—CAMEN, H. W.: J. Phys. F, *8*, 1978, p. 1525.

[18] LEE, E. W.—POURARIAN, F.: Phys. stat. sol. (a), *33*, 1976, p. 483.

[19] WADA, H.—YOSHIMURA, K.—KIDO, G.—SIGHA, M.—MEKATA, M.—NAKAMURA, Y.: Sol. State Commun., *65*, 1988, p. 23.