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Journal of Alloys and Compounds 303–304 (2000) 285–288

Journal of ALLOYS AND COMPOUNDS

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Evolution of the magnetic behavior of the Co subsystem in YCo_3 caused by small variations in stoichiometry and Al substitution

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Abstract

The phase composition at room temperature and the magnetization up to 55 kOe over the temperature interval 5–400 K for polycrystalline compounds $YCo_{3+\delta}$ ($-0.18 \le \delta \le 0.24$) and $Y(Co_{1-x}Al_x)_{2.92}$ ($x \le 0.1$) were studied. It was found that a homogeneous rhombohedral $PuNi_3$-type structure is formed within the Co concentration interval $-0.14 \le \delta < -0.08$. The magnetic ordering temperature, magnetization at 5.5 T, and the lattice parameters of $YCo_{2.88}$ were determined to be 260±2 K, 0.46±0.3 μ_B/Co and $a = 5.02$ Å, $c = 24.38$ Å (hexagonal set), respectively. The nonlinear variation of T_C vs. Al concentration was ascribed to the composition dependence of the Co magnetic moment.

Keywords: Magnetically ordered materials; Metals; Magnetization; Phase transitions

1. Introduction

The intermetallic compounds of rare earths (RE) with 3d elements, in which the 3d-itinerant subsystem shows a magnetic instability, are of current interest. Some of these compounds exhibit a magnetic instability in the itinerant electron subsystem and are characterized by a drastic change of the magnetic properties under a small variation of internal (atomic substitutions, interatomic distances, molecular fields) or/and external (pressure, magnetic field) parameters. The RCo_3 intermetallics ($PuNi_3$-type rhombohedral structure), in which the Co atoms occupy three non-equivalent positions (3*b*, 6*c* and 18*h*), hold a remarkable place since the magnetic instability is assumed to exist in more than one sublattice [1].

In YCo_3 with a non-magnetic RE, two successive metamagnetic transitions were observed under ultra-high external magnetic fields: a transition from a low (LMS) to an intermediate magnetic state (IMS) with $\Delta M_{Co} = 0.48$ μ_B/f.u.; followed by a transition from the IMS to a strongly magnetic state (SMS) with $\Delta M_{Co} = 1.05$ μ_B/f.u [1]. The ground state of the Co subsystem in RCo_3 depends on the strength of the f–d exchange interaction caused by magnetic RE elements. Different Co states induced by substitutions were observed in the $(Y,Gd)Co_3$ system, with $\Delta M_{Co} = 0.2$ and 1.2 μ_B/f.u. for LMS→IMS and IMS→SMS, respectively [2].

According to numerous data, the differences in the Curie temperature, T_C, and spontaneous magnetization, M_s, observed for different YCo_3 samples can reach 40 K and 0.8 μ_B/f.u., respectively. This scattering in the magnetic characteristics of YCo_3 can be caused by small variations of stoichiometry, which may induce a change of the Co magnetic state.

An important feature of the magnetically unstable compounds is a non-linear dependence of basic magnetic characteristics (magnetization, T_C, etc.) in regard to the 3d-electron concentration. In the $Y(Co,Al)_2$ system, a sharp 20- to 25-fold increase of the Curie temperature and a tripling of the magnetization were observed, which were ascribed to an increase of the density of d-states, $N(\varepsilon)$, at the Fermi level, ε_F, due to a decrease in the d-electron concentration [3]. Theoretical calculations have shown that $N(\varepsilon)$ of YCo_2 and YCo_3 have similar peculiarities near ε_F [4]. Therefore, a non-linear variation of T_C can also be

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0925-8388/00/$ – see front matter
PII: S0925-8388(00)00586-7

expected in YCo_3, owing to substitutions in the Co subsystem.

The aims of this work were to ascertain the homogeneity range for which single-phase $YCo_{3+\delta}$ compounds with the $PuNi_3$-type structure can be synthesized, and to follow the regularities in the evolution of M_s and T_C when changing the stoichiometry in YCo_3 and the Co concentration in the $Y(Co,Al)_3$ system.

2. Experimental procedure

The polycrystalline $YCo_{3+\delta}$ ($-0.16 \leq \delta \leq 0.12$) and $Y(Co_{1-x}Al_x)_3$ ($x \leq 0.1$) systems were prepared by arc melting constituent components under a protective argon atmosphere and annealing at 1000°C under dynamic vacuum for 48 h. X-ray powder diffraction and magnetic measurements were used to determine the phase composition of the compounds. The latter method allows one to detect ferromagnetic impurities at about the 10^{-3}% atomic concentration limit.

The magnetization up to 55 kOe and low-field DC susceptibility were measured using a SQUID magnetometer over the temperature range 5–400 K. The magnetization experiments were performed using powdered samples magnetized first under 55 kOe at room temperature and then cooled to 5 K, in order to avoid the influence of magnetocrystalline anisotropy. The transition temperatures were obtained from the maxima in the dM/dT curves.

3. Results and discussion

Fig. 1 shows a typical X-ray powder diffraction pattern of a YCo_3 sample. Small amounts of a foreign phase, either YCo_2 or Y_2Co_7, were detected for $\delta < -0.16$ and $\delta \geq 0.06$, respectively. Within the accuracy of the X-ray method, for the concentration range $-0.16 \leq \delta < 0.06$ the $YCo_{3+\delta}$ system contained the $PuNi_3$-type phase only. The lattice parameters of all the $YCo_{3+\delta}$ samples were constant and at values $a = 5.02$ Å and $c = 24.38$ Å (in the hexagonal set).

The magnetization curves of the $YCo_{3+\delta}$ intermetallics at 5 K are shown in Fig. 2. All the compounds show spontaneous magnetization. For $-0.16 \leq \delta \leq -0.06$, they exhibit almost the same behavior and the magnetization reaches 0.48 ± 0.03 μ_B/Co at the field 55 kOe, which corresponds to the LMS for the Co subsystem in RCo_3 intermetallics [1,2]. The small discrepancy in the magnetic behavior of this group can be related to the differences in the grain orientation of the powdered samples (texture). For positive values of δ, the magnetization of this system at 55 kOe starts to increase sharply and reaches the value 1.05 μ_B/Co for $\delta = 0.24$. Taking into account the results of the X-ray phase analysis (see Fig. 1), such an enlargement of the magnetization can be related to the increasing content of the ferromagnetic Y_2Co_7 phase with a higher magnetization value. The presence of a magnetic impurity for $\delta > -0.06$ can be detected in Fig. 3, where the temperature dependences of the magnetization for the $YCo_{3+\delta}$ and $Y(Co_{1-x}Al_x)_{2.92}$

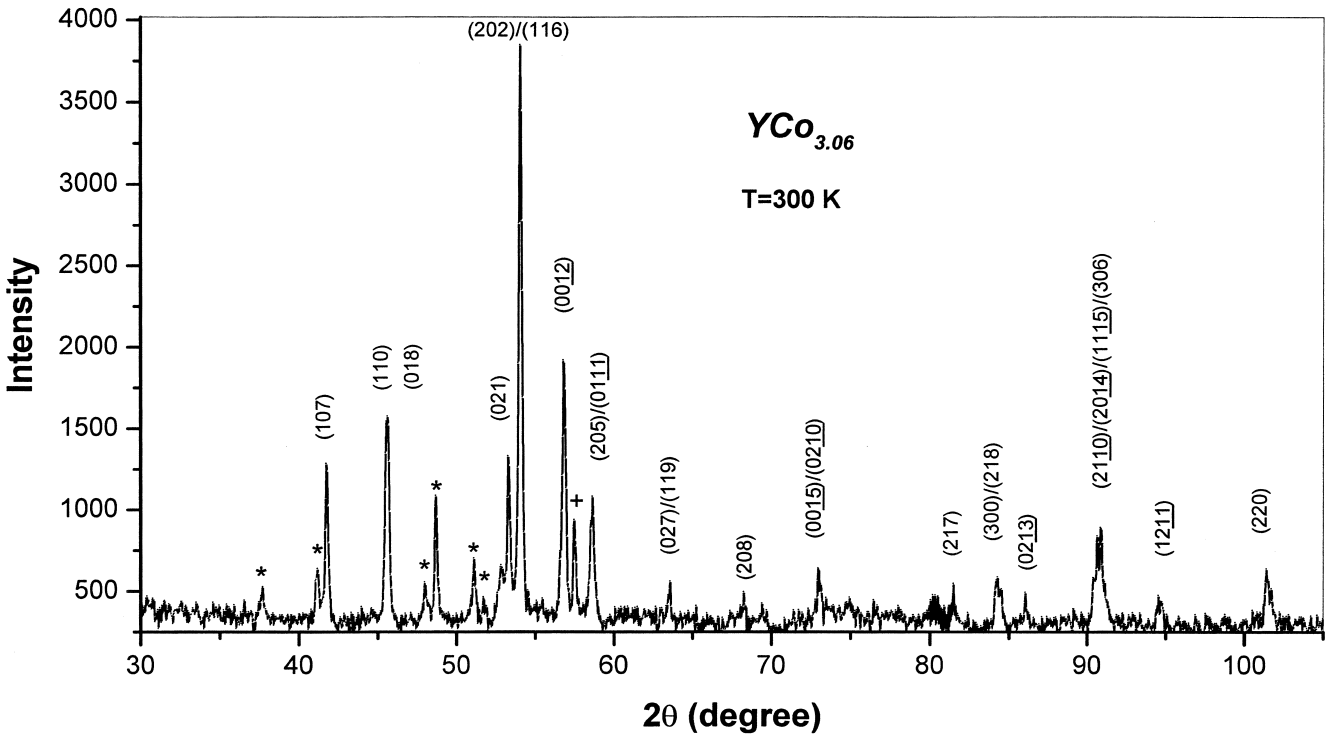

Fig. 1. X-ray diffraction pattern of the $YCo_{3.06}$ sample (Fe Kα radiation). (*) β-Lines of the YCo_3 phase; (+) main peak of the Y_2Co_7 impurity phase.

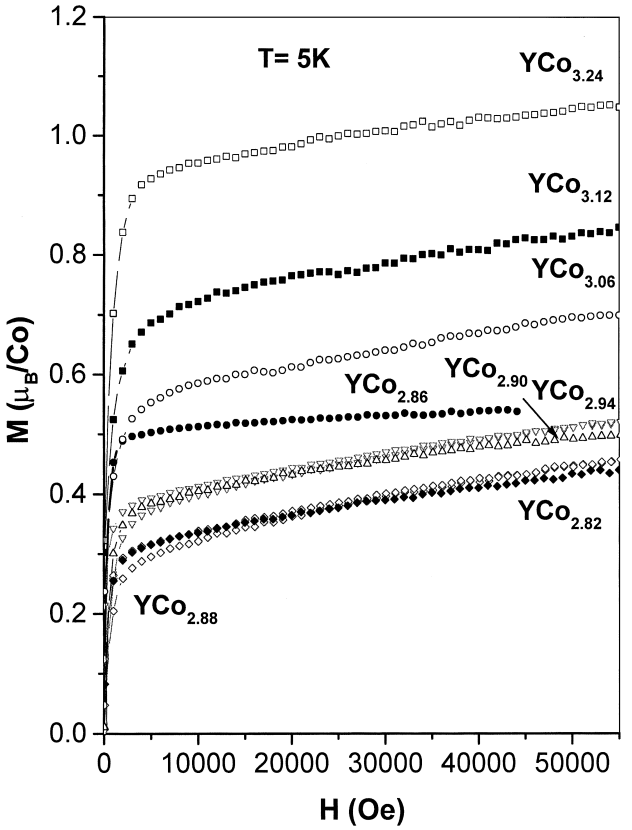

Fig. 2. Magnetization isotherms of the $YCo_{3+\delta}$ and $Y(Co_{1-x}Al_x)_{2.92}$ systems at 5 K.

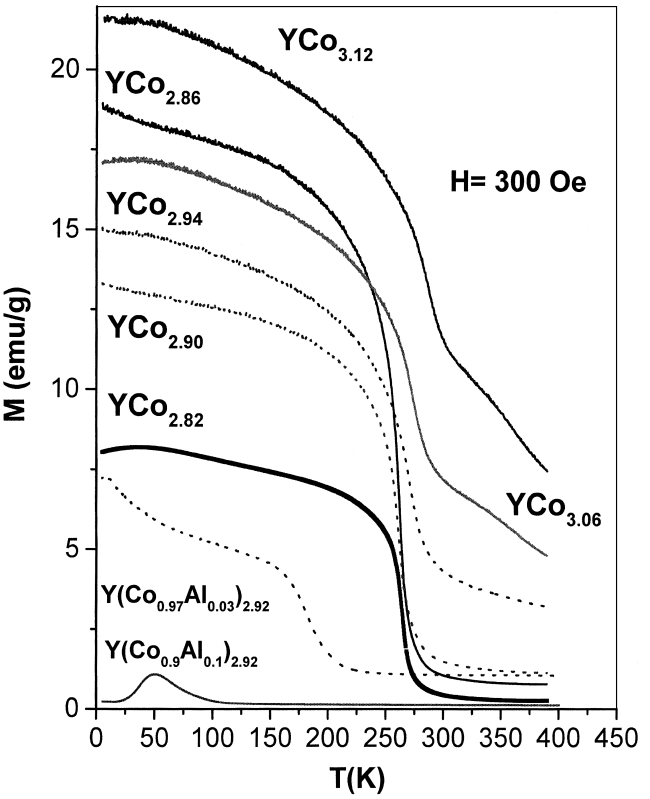

Fig. 3. Temperature variations of the low-field magnetization of the $YCo_{3+\delta}$ and $Y(Co_{1-x}Al_x)_{2.92}$ systems.

systems at low magnetic field (300 Oe) are presented. All of the $YCo_{3+\delta}$ intermetallics have the same Curie temperature, 260 K; however, the magnetization signal for the Co-rich compound ($\delta \geq -0.06$) above the Curie temperature is at least 10 times as high as that of the other intermetallics with $\delta < -0.06$. Y_2Co_7 has $T_C = 639$ K and $M_s = 1.06\ \mu_B$/Co [5]. Therefore, the presence of this compound can explain the observed increase of the magnetization above 270 K.

Substitution of Co by Al in YCo_3 results in a rapid reduction of T_C. The variation of T_C as a function of the Co concentration is given for the $YCo_{3+\delta}$ and $Y(Co_{1-x}Al_x)_{2.92}$ systems in Fig. 4. This figure is characterized by a non-linear decrease of T_C with increasing Al concentration. The value of T_C for the $YCo_{3+\delta}$ system does not change within the Co concentration interval 2.84–2.90 where single-phase $PuNi_3$-type samples were synthesized. When the sample contains ferromagnetic impurities ($\delta \geq -0.06$), some ''pseudo shift'' in T_C can be observed (due to the overlap of the $M(T)$ curves of YCo_3 and Y_2Co_7). Nevertheless, the low-temperature magnetization of the $YCo_{3+\delta}$ compounds is sensitive to δ in the $\delta \geq -0.06$ interval. The increase of the amount of impurity phase in the Co-rich intermetallics of the $YCo_{3+\delta}$ system can account for the sharp increase of magnetization at 5 K. Indeed, taking into account that the foreign phase

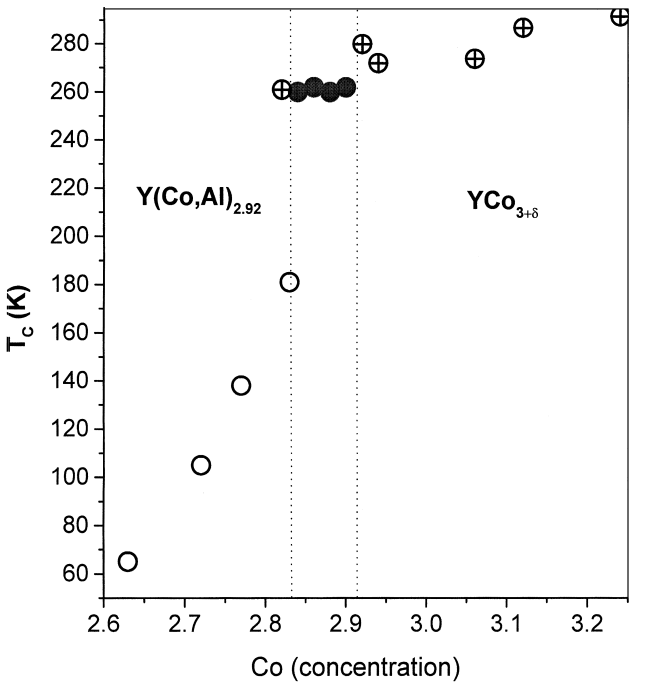

Fig. 4. Concentration dependence of T_C for the $YCo_{3+\delta}$ and $Y(Co_{1-x}Al_x)_{2.92}$ systems: (○) T_C for the $Y(Co_{1-x}Al_x)_{2.92}$ system; T_C of the single-phase (●) and non-single-phase (⊕) compounds of the $YCo_{3+\delta}$ system.

found by X-ray analysis in the sample $YCo_{3.24}$ is Y_2Co_7, the enhancement of the magnetization for 10% of impurity must be about 0.2 μ_B/Co.

Consider now the variation of the Curie temperature of the $Y(Co_{1-x}Al_x)_{2.92}$ system. For a very weak itinerant ferromagnet, a universal expression relating M_s and T_C can be written [6]:

$$M(0,0)/T_C = F(N^{(n)}(\varepsilon_F))$$

where the right-hand side is a function of the derivatives of $N(\varepsilon_F)$ with respect to energy and does not depend on the strength of the exchange interaction. Assuming the magnetic moment per Co atom is constant, $M_s(0,0)$ should vary linearly with x, $M(0,0) = 2.92(1-x)\mu_{Co}$. The strongly non-linear and sharp change of T_C indicates that the d-band characteristics of YCo_3 are extremely sensitive to substitutions; i.e. $N(\varepsilon)$ changes rapidly near ε_F. This is one of the basic features of itinerant electron metamagnets and is in agreement with theoretical band structure calculations of Ref. [4].

Acknowledgements

This work was supported by CARS, University of Chicago, by INTAS (Pr. 96-0630, EU) and RFBR Foundation.

References

[1] T. Goto, H. Aruga Katori, T. Sakakibara, M. Yamaguchi, Physica B 177 (1992) 255.
[2] H. Aruga Katori, I.S. Dubenko, I.Yu. Gaidukova, T. Goto, R.Z. Levitin, A.S. Markosyan, A.Yu. Sokolov, Physica B 211 (1995) 87.
[3] V.V. Aleksandryan, K.P. Belov, R.Z. Levitin, A.S. Markosyan, V.V. Snegirev, Pis'ma Zh. Eksp. Teor. Fiz. 40 (1984) 77, in Russian.
[4] M. Shimizu, J. Inoue, J. Magn. Magn. Mater. 54–57 (1986) 963.
[5] M.N. Baratashevich, A.V. Deryagin, N.V. Kudrevatykh, E.N. Tarasov, Zh. Eksp. Teor. Fiz. 84 (1983) 1140, in Russian.
[6] M. Shimizu, Rep. Prog. Phys. 44 (1981) 329.