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Spin reorientation and first-order magnetisation process in HoFe_{11-x}Co_xTi compounds

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Abstract

The influence of Co substitution for Fe on the lattice parameters, ordering temperature, saturation magnetisation, spin-reorientation temperature, and first-order magnetisation process (FOMP) of HoFe_{11-x}Co_xTi (x = 0.3, 0.7, 1, 3, 5, 7, 9, 11) compounds is investigated. The tetragonal crystal structure of the parent HoFe₁₁Ti does not change upon Co substitution, but the lattice parameters *a* and *c* decrease monotonically with the increase of Co content. The increase of x in HoFe_{11-x}Co_xTi compounds has a beneficial effect in improving the Curie temperature from 513 K in HoFe₁₁Ti to 983 K in HoCo₁₁Ti compound. The highest saturation magnetisation was observed in the compound with x = 3 at all measured temperatures. In HoFe_{11-x}Co_xTi compounds, with x = 0, 1, 3, 5, 7, a FOMP of type II occurs at fields less than 2T and below 100 K. In HoFe₂Co₉Ti and HoCo₁₁Ti compounds spin reorientations are observed at $T_{SR} = 260$ and 273 K, respectively.

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1. Introduction

Ternary intermetallic compounds of the type $RT_{11}M$ (R = rare earth elements, T = transition metal such as Fe,Co, Mn, and M = nonmagnetic element such as Ti, Mo, V, Cr, W, or Si) have been intensively investigated as candidates for permanent magnet applications. All these compounds crystallise in the tetragonal ThMn₁₂ structure with the space group I4/mmm and two formula units per unit cell [1–3]. Pseudo-ternary compounds of the type $RFe_{11-x}Co_xM$ also crystallise in the ThMn₁₂ structure. The influence of the Co concentration on the spin reorientations and magnetic anisotropy in $TbFe_{11-x}Co_xTi$ [4], and $RFe_{11-x}Co_xTi$ (with R = Dy, Er [5] and R = Y, Tb, Er [6]) compounds were investigated previously. By means of results obtained on the $YFe_{11-x}Co_xTi$ series, it has been shown that the sign of the anisotropy of the R sublattice as well as that of the 3d sublattice is concentration

dependent. Magnetic properties and magnetic structure of HoFe₁₁Ti have already been extensively studied [7–17], but HoFe_{11-x}Co_xTi compounds have received insufficient attention. In this work, the structure and magnetic properties of HoFe_{11-x}Co_xTi with x = 0, 0.3, 0.7, 1, 3, 5, 7, 9, 11 are investigated in details.

2. Experimental procedure

The HoFe_{11-x}Co_xTi polycrystalline samples were prepared by arc melting of the constituent materials (Ho, Fe, Co, Ti) of 99.9% purity under purified Ar atmosphere. Then, the buttons were re-melted in a high-frequency induction furnace equipped with a water-cooled copper crucible. To assure the homogeneity, the samples were subsequently wrapped into Ta foil, sealed into an evacuated quartz tube and annealed for 12 days at 1050 °C and then quenched in air. The X-ray diffraction diagrams showed that the annealed samples were approximately single phase. The amount of impurity phases was below about 5%. Magnetically oriented powders were also

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examined by X-ray diffraction, in order to establish the easy direction of magnetisation at room temperature.

The Curie temperatures of the samples, being sealed in a silica tube to avoid oxidation, were determined by a setup based on the Faraday technique, with the accuracy of the temperature and magnetisation measurements of $\pm 0.1^{\circ}$ and 0.001a.u., respectively. Magnetisation measurements of the powder samples, being pressed in a sample holder with a piece of tissue on the top to avoid free rotation of the particles, were performed at 5, 50, 100, 150, 200, and 300 K by the extracting sample magnetometer in a superconducting field up to 10 T. Spin reorientation temperatures, of the powder particles, were determined from magnetisation vs. temperature curves, ranging from 5 to 300 K in a constant field of 100 mT.

3. Results and discussion

3.1. Crystallographic results

Results of X-ray diffraction revealed the formation of approximately single-phase materials for the entire composition range in the HoFe_{11-x}Co_xTi alloy system. They crystallise in the characteristic tetragonal ThMn₁₂ structure (space group I 4/mmm). Introduction of cobalt in the lattice of the former alloy resulted in a decrease of the lattice parameters. This is expected, due to the smaller size of the cobalt atom compared to that of iron. The decrease of the lattice parameters *a* and *c* with the increase of Co content is found to be linear, but the parameter *a* decreases faster than *c*. Going from HoFe₁₁Ti to HoCo₁₁Ti, the parameter *a* decreases as much as 0.528 Å, while the parameter *c* decreases only 0.075 Å.

A typical X-ray powder diffraction pattern for HoFe₆Co₅Ti is presented in Fig. 1. Results of the structural data are presented in Table 1 and displayed in Fig. 2. Treatment of the X-ray data was carried out using the FULLPROF program.



Fig. 1. A typical X-ray powder diffraction pattern for HoFe₆Co₅Ti.

Table 1 Lattice parameters *a*, *c* and the cell volume *V* for various $HoFe_{11-x}Co_xTi$ compounds

X	<i>a</i> (Å)	<i>c</i> (Å)	$V(\text{\AA}^3)$
0.0	8.491	4.784	344.91
0.3	8.488	4.782	344.52
0.7	8.485	4.779	344.07
1.0	8.482	4.777	343.68
3.0	8.462	4.763	341.06
5.0	8.441	4.750	338.44
7.0	8.422	4.736	335.92
9.0	8.402	4.723	333.41
11	8.382	4.709	330.84

It has been established that in HoFe₁₁Ti structure the Ho atoms occupy the corners and the centres of the tetragonal cell (2a). The Fe atoms occupy one or more positions 8i(x, 0, 0), 8j(x', 0, 1/2), 8f(1/4, 1/4, 1/4) shown in Fig. 3. Because of a most favourable heat of formation of Fe–Ti than Ho–Ti binaries, the Ti atoms occupy preferentially the 8i sites [11]. Because also of the smallest atomic 8f volume (in comparison with those of 8i and 8j sites), Co atoms at first occupy 8f sites to form two direct Co–Ho bands, then they occupy 8j and 8i sites, respectively [17].

3.2. Curie temperature

Magnetisation vs. temperature curves for $HoFe_{11-x}Co_x$ Ti compounds are displayed in Fig. 4. Curie temperatures of compounds were determined from the second derivative of magnetisation vs. temperature plots and are presented in Table 2. For all the studied HoFe_{11-x}Co_xTi compounds, the Curie temperature increases with cobalt content nonlinearly (Fig. 5). The maxim increase in Curie temperature is 105 K for increasing x from zero to one, and the minimum increase is only 3 K for increasing x from 9 to 11. It is also evident from the curves in Fig. 5 that the magnetisation value below Curie temperature is higher than zero and in some samples even show a second transition above 1000 K. This is due to the presence of the second or even third magnetic phases in the samples. The Bragg peaks of the impurity phases were also observed in the X-ray diffraction diagrams, but no attempt was made for their identifications.

In terms of the exchange interactions (or molecular field coefficients) the M–M (M=Co or Fe) contribution of the exchange interaction, i.e. J_{M-M} , to the Curie temperature is dominant in comparison to the J_{Ho-M} one, whereas J_{Ho-Ho} contribution can be neglected. This is well expressed by [18,19]

$$T_{\rm C} = \frac{1}{2} \left(T_{\rm M} + \sqrt{T_{\rm M}^2 + 4T_{\rm Ho-M}^2} \right),$$

where $T_{\rm M} = A J_{\rm M-M} S(S+1)$ and $4T_{\rm Ho-M} = B J_{\rm Ho-M} G_J S(S+1)$, A and B being constants within a series of compounds. $G_J = (g_J - 1)^2 J (J+1)$ is the "de Gennes" factor. S is

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