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Crystal structure, electrical resistivity and Curie temperature of $Ho(Mn_{1-x}Fe_x)_2$ and $Ho(Co_{1-x}Ni_x)_2$ intermetallics

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ABSTRACT

Synthesis of $Ho(Mn_{1-x}Fe_x)_2$ and $Ho(Co_{1-x}Ni_x)_2$ intermetallic compounds, studies of their crystal structure and electrical resistivity were carried out.

A pure cubic Fd3m, C15, $MgCu_2$-type Laves phase was evidenced by X-ray measurements for all compounds. The unit cell parameter decreases nonlinearly with composition parameter x (or the average number n of 3d electrons per transition metal atom).

Electrical resistivities for $Ho(Mn_{1-x}Fe_x)_2$ and $Ho(Co_{1-x}Ni_x)_2$ compounds were measured in a wide temperature range (13–1000 K) and, for most of them, the component resistivities: residual, phonon and magnetic were separated. The parameters characterising the dependence of resistivity on temperature and composition, including the Debye temperature, were determined. The differential of the magnetic part of electrical resistivity against temperature was used to estimate Curie temperatures. The Curie temperature grows with an increasing amount of iron for $Ho(Mn_{1-x}Fe_x)_2$ compounds, and for $Ho(Co_{1-x}Ni_x)_2$ it reduces with an increasing amount of nickel.

All results are summarized together with those for the $Ho(Fe_{1-x}Co_x)_2$ series, which have been presented previously.

1. Introduction

Heavy rare earth (R)–transition metal (M) compounds of the RM_2 type have been investigated extensively for scientific and application purposes [1–5]. The origin of the magnetic and electrical properties of these materials has been an enduring subject of interest.

Heavy rare earth–transition metal compounds are ferrimagnets, due to the coexistence of 4f(5d) and 3d electron magnetism [6–8]. Both the 4f5d electrons of the rare earth sublattice and the 3d band-type electrons of the transition metal sublattice are a source of the magnetic properties of R–M intermetallics. The influence of 3d electrons is predominant [7–10].

Previously, the results of changing the number of 3d electrons (caused by Fe/Co substitution) in the transition metal sublattice have been studied in $Ho(Fe_{1-x}Co_x)_2$ compounds using Mössbauer effect and electrical resistivity measurements [9–12]. In those papers, it was proven that both hyperfine magnetic fields and magnetic ordering temperatures resemble Slater–Pauling type curves.

This paper extends electrical resistivity studies to the neighbouring $Ho(Mn_{1-x}Fe_x)_2$ and $Ho(Co_{1-x}Ni_x)_2$ intermetallic substituted series.

To this end, electrical resistivity measurements on the series $Ho(Mn_{1-x}Fe_x)_2$ and $Ho(Co_{1-x}Ni_x)_2$ were performed in a wide range of temperatures and the Curie and Debye temperatures were determined. The data are compared with those known for the $Ho(Fe_{1-x}Co_x)_2$ series and with data known for other intermetallics.

The average number n of 3d electrons per transition metal atom can be calculated for $Ho(K_{1-x}L_x)_2$-type compounds using the following formula: $n = n_K(1-x)+n_L x$, where n_K is the number of 3d electrons per first transition metal atom, n_L number per second atom, giving a stoichiometric formula, specifically $n_{Mn} = 5$, $n_{Fe} = 6$, $n_{Co} = 7$, $n_{Ni} = 8$ [13].

2. Materials and X-ray studies

Polycrystalline materials $Ho(Mn_{1-x}Fe_x)_2$ (for composition parameter x=0, 0.2, 0.4, 0.6, 0.8) and $Ho(Co_{1-x}Ni_x)_2$ (x = 0.05,0.1,0.2,0.4,0.6,0.8,1) were synthesized by arc melting with contact-less ignition in a high purity argon atmosphere, applying appropriate amounts of Ho (99.95% purity), Mn, Fe, Co and Ni (all 99.999% purity) metals [14]. The obtained ingots were annealed in vacuum at 1200 K for 1 h and then cooled down along with the furnace (approximate cooling rate: 400 K/h).

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The crystal structure of the post-annealed compounds was studied with standard X-ray powder diffraction measurements using MoK_α radiation at room temperature. The X-ray diffractograms (Figs. 1 and 2—points) measured for these compounds were numerically analyzed using a Rietveld-type procedure (fitted lines, Miller indexes, pairs of sticks related to X-ray peaks and differential pattern) adopting both $K_{\alpha 1}$ (wavelength $\lambda_1 = 0.70930$ [Å]) and $K_{\alpha 2}$ (wavelength $\lambda_2 = 0.71359$ [Å]) X-ray lines [15,16]. All compounds of the tested series showed a clean cubic Laves phase with an Fd3m, $MgCu_2$-type, C15 crystal structure. The C15-type Laves phase has been described in detail elsewhere [17].

As the atomic radius of the transition metal atom, starting from Mn and ending at Ni, decreases: $r_{Mn} = 1.79$ [Å], $r_{Fe} = 1.72$ [Å], $r_{Co} = 1.67$ [Å] and $r_{Ni} = 1.62$ [Å] [13], so the determined unit cell parameter a reduces with parameter x (or n) (Fig. 3). For the $Ho(Mn_{1-x}Fe_x)_2$ intermetallic series, cell parameter a decreases softly non-linearly and can be ascribed the following numerical formula: $a(x) = (7.540 - 0.284x + 0.057x^2)$ [Å] (curve 1 in Fig. 3). For the $Ho(Fe_{1-x}Co_x)_2$ compounds experimental points and curve 2 (Fig. 3) were repeated after [11]. For the $Ho(Co_{1-x}Ni_x)_2$ intermetallics, cell parameter a decreases almost linearly and can be approximated by the numerical formula: $a(x) = (7.180 - 0.029x)$ [Å] (curve 3 in Fig. 3). These formulae, which were obtained by using a least squares fitting procedure, follow the experimental points satisfactorily. The maximal error Δa of experimental points equals 0.005 [Å]. Selected values $a(x)$ of the series coincide satisfactorily with the existing literature data (open squares in Fig. 3) [1,18–22]. The concave and convex deviations $a(x)$ from Vegard's rule, which are typical of $R-M$ intermetallics, can presumably be ascribed to a magnetovolume effect.

Generally, the whole $a(n)$ dependence for $Ho(Mn_{1-x}Fe_x)_2$, $Ho(Fe_{1-x}Co_x)_2$ and $Ho(Co_{1-x}Ni_x)_2$ intermetallic series, is approximately exponential in nature, as shown in the insert in Fig. 3. Considering the experimental points for $Ho(Mn_{1-x}Fe_x)_2$ and $Ho(Co_{1-x}Ni_x)_2$, the following exponential function was fitted by: $a(n) = (7.092 + 19.708\exp(-0.753n))$ [Å] (curve 4, insert in Fig. 3).

3. Measurements of resistivity

Electrical measurements were performed on parallelepiped shaped specimens with typical dimensions of 1 mm × 1 mm× 10 mm. Specimens were precisely cut from ingots using a diamond wheel saw. The electrical contacts to the bars were attached by point spark-welding of high purity thin copper wires onto the ends of the bars. Microscopically observed crack free specimens were used for the resistivity measurements.

Electrical resistivity was measured using a four probe method. The obtained good quality electrical resistivities ρ as functions of

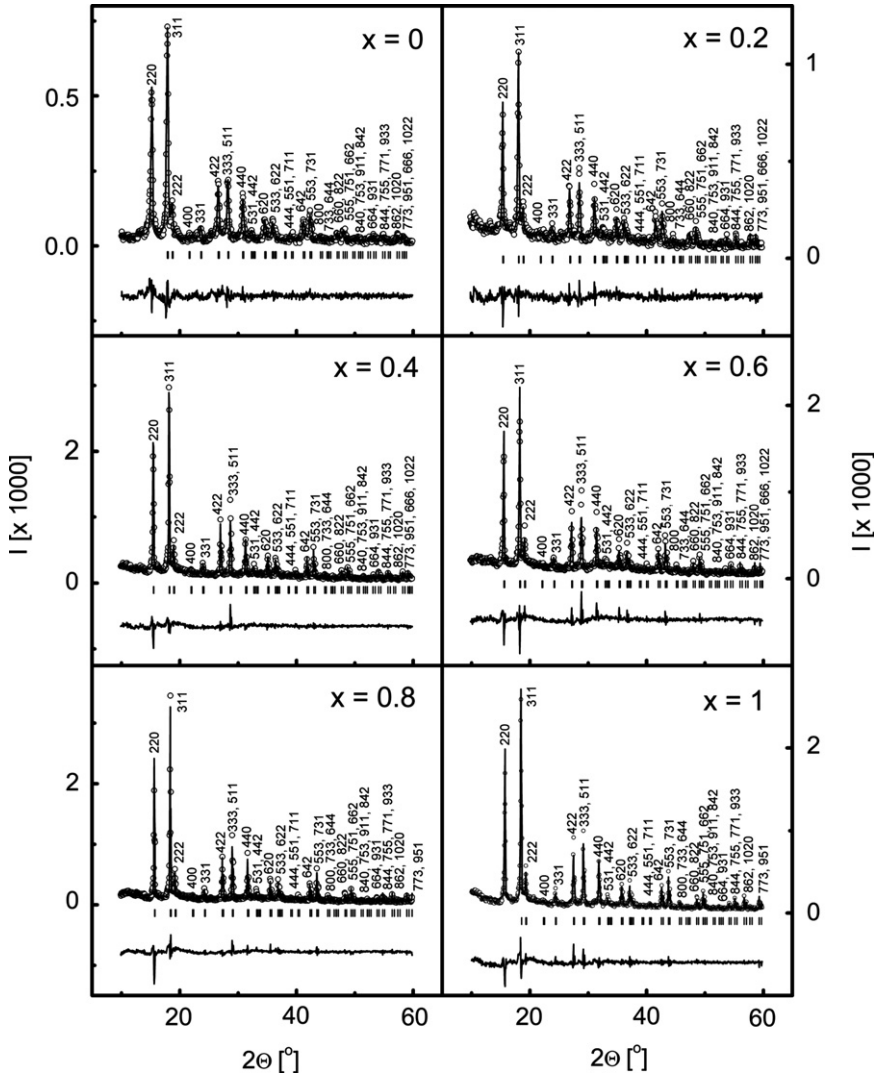

Fig. 1. X-ray patterns of the $Ho(Mn_{1-x}Fe_x)_2$ intermetallic series at 295 K. Pattern for $HoFe_2$ repeated after [11].