Materials Science and Engineering B 193 (2015) 76–82

Contents lists available at ScienceDirect

Materials Science and Engineering B

journal homepage: www.elsevier.com/locate/mseb

# Electrical and magnetic properties, and FLAPW electronic band structure of magnetostrictive $Tb_{0.27}Dy_{0.73}(Fe_{0.7-x}Ni_xCo_{0.3})_2$ compounds

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ARTICLE INFO

*Article history:*
Received 29 July 2014
Received in revised form 9 November 2014
Accepted 18 November 2014
Available online 27 November 2014

*Keywords:*
Intermetallic compounds
Debye–Scherrer powder method
Rietveld analysis
Electrical properties
Magnetic properties
Band structure calculations

ABSTRACT

The structural and physical properties of nickel-diluted $Tb_{0.27}Dy_{0.73}(Fe_{0.7-x}Ni_xCo_{0.3})_2$ intermetallics were studied by X-ray diffraction, four-probe dc electrical measurements and standard strain gauge method. X-ray analysis shows that all samples crystallize in a cubic Laves structure. The lattice parameter decreases linearly with the nickel content. Electrical resistivity was measured in a temperature range of 15–1100 K. The parameters involved in the dependence of resistivity on temperature and composition were determined. Residual, phonon and magnetic resistivity were separated from the electrical resistivity using both the Matthiessen and Bloch-Grüneisen formulas. The compounds' Curie temperatures, which decrease nonlinearly with $x$, were obtained from the magnetic resistivity curves. The maximum values of magnetostriction attained for the $Tb_{0.27}Dy_{0.73}(Fe_{0.6}Ni_{0.1}Co_{0.3})_2$ compound exceed about 851 ppm. Electronic 3d-band structure and magnetic moment calculations were performed using the Full-Potential Linearized Augmented Plane Waves method. The distribution function for the densities of 3d-states was used to characterise the transition metal subbands.



## 1. Introduction

$RM_2$-type compounds, some of the most important smart magnetic materials, have only recently found their way into actuators in applications requiring large displacements and as sensors in applications including broadband shakers, surgical instruments, ultrasonic transducers, hearing aids, load cells, accelerometers, proximity sensors, torque sensors and magnetometers [1,2]. $RFe_2$-type intermetallics have recently been widely studied as magnetostrictive constituents of the magnetoelectric composites [3–6], which have potential applications in transducers, spintronics, information storage and sensors [7].

At the atomic level, magnetostriction is related to the magnetic properties (magnetisation, magnetic moment, anisotropy) of materials. The magnetism in R–M intermetallics and the competitive effect between different magnetic interactions in rare earth and transition metal subblattices are still a field open to fundamental investigation. The magnetism of rare earth-transition metal intermetallics results from the coexistence of the exchange interactions between the 4f(5d) electrons of the rare earth sublattice and the 3d band-type electrons of the transition metal sublattice [8–13]. Substituting one transition metal atom with another in the $RM_2$ compounds can be treated as a driving force in changing the number of 3d electrons. Doing so changes the band structure, magnetic properties and the hyperfine interactions. Previous investigations have shown that the magnetostriction of the $RFe_2$ compounds can be significantly changed when Fe is replaced by other transition metals. Considerable work substituting Fe/Co has been done in an effort to improve the magnetic properties and magnetostriction of cubic $RFe_2$ compounds [14–16]. Specifically, this substitution increases the Curie temperature, magnetic moments, hyperfine interactions and magnetostriction of the $R(Fe_{1-x}Co_x)_2$ compounds ($R = Tb_{0.27}Dy_{0.73}$, $Nd_{0.9}Tb_{0.1}$, $Pr_{0.5}Nd_{0.5}$). It has been found that maximum values of the magnetic hyperfine field, Curie temperature and magnetic moment are observed for the $Tb_{0.27}Dy_{0.73}(Fe_{0.7}Co_{0.3})_2$ compound. It has also been reported that the small substitution of Ni for Fe can increase magnetostrictive properties, but reduces the magnetic hyperfine field, magnetic moment and Curie temperature in R–M intermetallics [17–19].

In contrast to the magnetic properties, the electrical and magnetostrictive properties of the investigated system are less known and the origin of these properties and their relations to

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http://dx.doi.org/10.1016/j.mseb.2014.11.013
0921-5107/

magnetism and electronic band structure would seem still to be an open topic for research. In this work, we report the effect of substituting Ni for Fe in a $Tb_{0.27}Dy_{0.73}(Fe_{0.7}Co_{0.3})_2$ system. New, polycrystalline materials were synthesised by arc melting. X-ray analysis, electrical resistivity measurements and electronic band structure calculations using the Full-Potential Linearized Augmented Plane Waves (FLAPW) method were then done for the complete $Tb_{0.27}Dy_{0.73}(Fe_{0.7-x}Ni_xCo_{0.3})_2$ series. The contributions to total electrical resistivity for the $Tb_{0.27}Dy_{0.73}(Fe_{0.7-x}Ni_xCo_{0.3})_2$ series were separated for the first time. The FLAPW results relating to the statistical properties of the transition metal sublattice are used to describe the Curie temperature dependence on Fe/Ni substitution.

## 2. Materials and methods

Ingots with $Tb_{0.27}Dy_{0.73}(Fe_{0.7-x}Ni_xCo_{0.3})_2$ $(0 \le x \le 0.7)$ stoichiometry were synthesised by melting the constituent metals in an arc furnace in a high purity argon atmosphere. Appropriate amounts of Tb (99.9% purity), Dy (99.9% purity), Fe (99.99% purity), Ni (99.99% purity) and Co (99.99% purity) were used as starting materials. To achieve a better chemical homogeneity, the samples were re-melted twice. The synthesised samples were then annealed in vacuum at 1123 K for 2 h and cooled with a furnace.

Conventional X-ray powder diffraction analysis (TUR-M61, E. Germany) was carried out using $MoK_\alpha$ radiation at room temperature. Bar (cuboid)-shaped specimens (typically $1 \times 1 \times 10\,mm^3$) for the four probe dc electrical measurements were precisely cut from ingots using a diamond wheel saw. The electrical contacts to the bars were connected by point spark welding thin, high-purity copper wires onto the ends of the bars. Only samples verified by microscope to be crack-free were used for the electrical resistivity measurements. The magnetostriction was measured using the standard strain gauge method. After polishing and cleaning the sample surfaces, a flexible strain gauge was fastened to the surface using cyanoacrylate glue. The magnetostrictive strain was measured using a standard resistant Strain Gauge Meter. The samples with strain gauge were placed parallel or perpendicular to the static magnetic field. A Wheatstone bridge electrically connected with a DP40 strain meter was used to measure both the parallel and perpendicular magnetostrictions. The resolution in measuring the magnetostriction was better than 2 ppm. The electronic band structures of the $Tb_{0.27}Dy_{0.73}(Fe_{0.7-x}Ni_xCo_{0.3})_2$ series were calculated using ab-initio self-consistent Full-Potential Linearized Augmented Plane Waves (FLAPW) method as implemented in the WIEN2K code [20]. The FLAPW method is one of the most accurate first-principles methods for determining the structural, electronic and magnetic properties of materials. The exchange-correlation potential within the generalised gradient approximation (GGA) is calculated using the scheme of Perdew–Burke–Ernzerhof [21]. GGA + U method was used for 4f electrons including the on site correlation energy $U = 7$ eV to settle the energy scale of the Tb and Dy 4f electronic states [22–25]. A Brillouin zone integration was performed using a $k$ mesh of $280k$ points in the irreducible Brillouin zone wedge. The states of the core were treated relativistically, while the valence states were treated within a scalar relativistic approximation. A supercell approach was applied, with the supercell equivalent to eight crystal unit cells. During the calculations Fe, Co and Ni atoms were randomly distributed among the sites of the M-sublattice. Moreover, the numbers of Fe, Co and Ni atoms inside the supercell correspond to the stoichiometry of the computed compound. The charge and energy convergence limits were set to $10^{-7}$ e and eV, respectively. The same method of calculations was used previously by [18,22,26,27].

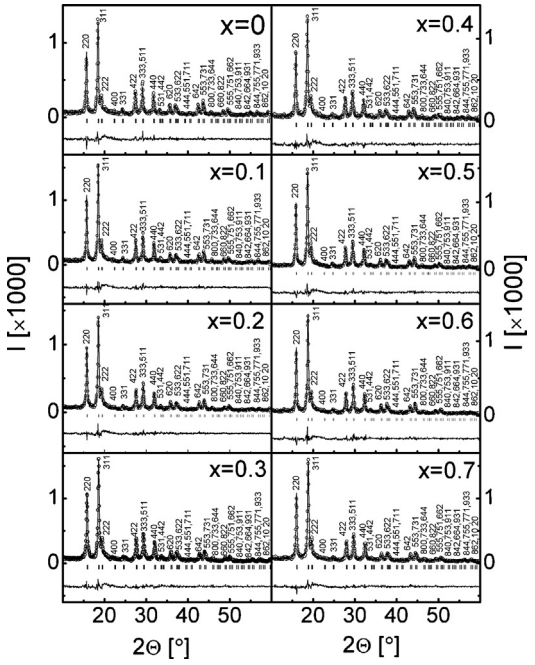


**Fig. 1.** X-ray powder diffraction patterns observed for the $Tb_{0.27}Dy_{0.73}(Fe_{0.7-x}Ni_xCo_{0.3})_2$ intermetallics (300 K). The fitted differential pattern is added below each diffractogram.

## 3. Results and discussion

### 3.1. Crystal structure

Good quality X-ray diffractograms (the patterns are presented in Fig. 1) obtained at room temperature for synthesized materials were analyzed using a Rietveld-type method [28,29]. Analysis of the diffractograms revealed a single-phase composition. The crystal structures of the materials stabilised in a cubic Laves Fd3m, $MgCu_2$-type structure. The $C15$ Laves phase has been described in detail elsewhere [30].

Fig. 2 shows the dependence $a(x)$ observed for the $Tb_{0.27}Dy_{0.73}(Fe_{0.7-x}Ni_xCo_{0.3})_2$ series (black points). The unit cell parameter $a$ linearly reduces with nickel content $x$. In practice, Vegard's rule is obeyed – because Ni atoms, which possess slightly smaller atomic radius ($r_{Fe} = 1.72$ Å, $r_{Ni} = 1.62$ Å) [31], were substituted for the Fe atoms. The data from the literature for $Tb_{0.27}Dy_{0.73}(Fe_{0.7}Co_{0.3})_2$ and $Tb_{0.27}Dy_{0.73}(Fe_{0.7}Ni_{0.3})_2$ compounds (open points) [14,26,32,33] coincide satisfactorily with our experimental data. The average number $n$ of 3d electrons (Fig. 2, upper axis) is calculated using expression $n = 6 \cdot (0.7 - x) + 7 \cdot x + 8 \cdot 0.3$ taking into account the stoichiometry of the series, where 6, 7 and 8 are the numbers of 3d electrons per Fe, Co and Ni atom, respectively.

Substituting one metal for another in the transition metal sublattice introduces a random distribution of atoms over crystallographic sites. Such a distribution of transition metal atoms allowed the $^{57}Fe$ Mössbauer effect spectra collected for the system considered here to be fitted successfully [27]. The random distribution of Fe, Co and Ni atoms for the series, the probability of two iron atoms occurring as nearest neighbours, or the probability of an Fe–Fe magnetic connection occurring can be calculated as $p_{Fe-Fe} = (0.7 - x)^2$. Analogously, the probabilities of other M–M nearest neighbourhoods of two atoms can be expressed as $p_{Fe-Co} = 2 \cdot (0.7 - x) \cdot 0.3$, $p_{Co-Co} = (0.3)^2$, $p_{Fe-Ni} = 2 \cdot (0.7 - x) \cdot x$, $p_{Co-Ni} = 2 \cdot 0.3 \cdot x$ and $p_{Ni-Ni} = x^2$ [34] and $p_{ij} = p_{ji}$. These probabilities will be useful in describing the experimental data that now follow.