The analysis of the magnetic properties and the electronic structure in the $Tb_xGd_{1-x}Fe_3$ intermetallics

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ABSTRACT

The polycrystalline compounds $Tb_xGd_{1-x}Fe_3$ with a $PuNi_3$ − type of crystal structure have been obtained. Based on wide-range SQUID magnetometer series of different magnetic measurements have been carried out. Moreover, magnetic properties in the paramagnetic range have been studied by means of the Faraday type magnetic balance. The partial replacement of Gd by Tb (Gd/Tb) atoms is reflected in the increase of magnetic parameters e.g. the increase of the saturation magnetic moment (M_S) from 1.6 μ_B/f.u ($x = 0.0$) to 3.42 μ_B/f.u ($x = 1.0$). The study of the hysteresis loops has been performed in several chosen temperatures. A quite strong dependence of coercivity (H_C) and remanent magnetization (M_r) on the temperature and the amount of Tb has been found. The exchange coupling parameters of R−R (A_{RR}), T−T (A_{TT}) and R-T (A_{RT}) have been evaluated from magnetization curves $M(T)$ based on the mean field theory (MFT) calculations. The XPS spectra have been measured at the room temperature. The valence band spectra as well as the core level lines have been analyzed as the influence of Gd/Tb substitution on the electronic structure. The valence bands near the Fermi level (E_F) are dominated by Fe3d states and indicate the increase of intensity of states for higher terbium content. A strong dependence of the magnetic properties on the changes within the electronic structure has been found.

1. Introduction

The R-T compounds where R is rare earth and T is a transition metal show very interesting magnetic properties due to the combination of 3d itinerant and 4f localized magnetism. One of the most know series is RNi_3 [1–14]. The analysis of its magnetic properties shows that the Curie temperatures are very low in comparison to other RT_3 compounds. One of the first studies of this series have been done by *Paccard and Pauthenet* [4] and concerns $GdNi_3$ compound. Magnetic measurements performed for this compound show that it is a ferrimagnet with saturation magnetic moment 6.55 μ_B/f.u. and the Curie temperature $T_C = 116$ K [1,4]. Similar values were obtained in later investigations made by *Greedan* [5] and *Burzo* [8,9] where the magnetic moment equals 6.6 μ_B/f.u. and 6.9 μ_B/f.u. respectively. Partially replacing of Ni atoms by other 3d elements leads to some changes in magnetic properties correlated with their electronic structure [1,5,8,10–13].

The second most known RT_3 series is RFe_3 [1,7–9,12,13]. All these compounds, except YFe_3 and $SmFe_3$ which are ferromagnets,

indicate the ferrimagnetic arrangement with a compensation point where total magnetization of the R and T magnetic sublattices equals zero or nearly zero [7].

Although in these materials rare earths occupy two non-equivalent positions, the results suggest that in fact the R and Fe moments are almost collinear. Since the magnetization observed at a compensation point (T_{comp}) is the highest for the $TmFe_3$ compound it is assumed that deviation from collinearity is the largest in this case.

The molecular field theory applied by *Herbst* et al. [7] exhibits that the magnitude of R-3d interactions based on the molecular field coefficients is stronger than R−R but weaker than the 3d−3d interactions in all studied RFe_3 compounds except $GdFe_3$ and $TbFe_3$. Thus, the high Curie temperatures (T_C) confirm the dominant role of iron 3d exchange interactions.

In the ferrimagnetic $GdFe_3$ compound the existence of the compensation point between magnetic moments of Gd and Fe sublattices was evidenced at 618 K. The average magnetic moment per iron atom was evaluated as about 1.8 μ_B and $T_C = 729$ K [5,8,9,12,13]. For the $TbFe_3$ compound T_C is lower and equals 648 K [1,7].

The magnetic properties in the RFe_3 series strongly depend on R atom. As it was previously reported the magnetic moment of iron

varies with R, e.g. in the case of DyFe$_3$, HoFe$_3$ and YFe$_3$ compounds equals 1.94 μ$_B$, 1.73 μ$_B$ and 1.67 μ$_B$ respectively [1,7,10,11,15]. The substitution within rare earth sublattice may lead to the changes of f–f interactions which are mostly realized by $5d$–$3d$ hybridization.

Moreover, it was shown that the change in $3d$ electron number has a strong influence on RFe$_3$ properties [5,6,10,11]. Thus a series of the R(Fe$_{1-x}$T$_x$)$_3$ compounds where R = Gd, Ho, Dy, Y and T = Ni, Co were studied [5,6,11–13]. The variation of the $3d$ magnetic moment with x may be explained on the base of the rigid band model [11]. It is well known that pure iron atom has 2.6 holes in the $3d$-band with the minority spins and 0.3 holes in the $3d$-band with majority spins. The Fermi level (E_F) is located at a minimum of density of states as long as the holes in the $3d$ − majority band are not filled. When this band is filled then the $3d$ minority band occupation increases. In the case of RFe$_3$ compounds the valence electrons of the rare earth can fill $3d$ band in the manner described above resulting in 5.7 holes [11]. The Fe/Ni substitution involves a further fulfillment within $3d$ minority band. As a consequence for Ni-rich compound d band is fulfilled.

Previously some of R$_x$Gd$_{1-x}$Fe$_3$ (e.g. R = Y) were studied [8,9]. As it has been shown by the authors the variation of T_C versus x is almost linear and the magnetic moments of gadolinium and iron sublattices are compensated for $x \approx 0.76$. It was assumed that the yttrium is non-magnetic and the two-sublattice model has been used. By this approach and taking into account the experimental results it was found that the interaction between iron atoms is the key to explain $T_C(x)$ dependence.

One of the tool useful in the analysis of the magnetic interactions is the mean field theory (MFT). By fitting the experimental $M(T)$ dependence it can be possible to determine the exchange coupling parameters of R−R (A_{RR}), T−T (A_{TT}) and R-T (A_{RT}) [16–21]. As it has been previously shown for some RT$_3$ as a result of substitution magnetic Gd by non-magnetic Y the magnetic interaction within $3d$ sublattice is quite large [22]. In the case of Tb$_x$Gd$_{1-x}$Ni$_3$ where another magnetic component was introduced into $4f$ sublattice with the increase of the x parameter the magnetic moment of Tb increases and antiparallel aligned magnetic moment of Ni atoms decreases [14]. Here, the T−T interaction has a slight influence on $M(T)$ dependence and only R − R and R − T interactions seem to be important. Moreover, $T_C(x)$ dependence can be proportional to a combination of A_{RR} and A_{RT} parameters but interaction within $4f$ site is almost 8 times stronger than the interactions between the two antiferromagnetically coupled magnetic sublattices R-T.

By a complementary study of both the magnetic properties and electronic structure it is possible to explain the mechanisms responsible for the observed results. Additionally, MFT theory may be useful in explaining the role of f − d interactions in the studied system. Thus, in the presented paper we are focused on influence of Tb substitution on the crystal and electronic structure as well as on magnetic properties of the Tb$_x$Gd$_{1-x}$Fe$_3$ compounds. The obtained results are novel and are presented for the first time.

2. Experimental details

The Tb$_x$Gd$_{1-x}$Fe$_3$ polycrystalline (x = 0.0, 0.1, 0.2, 0.4, 0.5, 0.6, 0.8, 1.0) samples were prepared by arc-melting from high purity elements (Tb − 99.9 wt.%, Gd − 99.9 wt.%, Fe − 99.99 wt.%.) under argon atmosphere. The melted samples were then wrapped in tantalum foil, placed in quartz tubes and annealed at 900 °C for one week. After annealing all the samples were single phase. The crystal structure of all samples was checked by means of X-ray diffraction (XRD) using Siemens D5000 diffractometer. The radiation used is copper K$_{\alpha 1}$ with a wavelength 1.54056 Å.

Magnetic properties of examined samples were measured with the use of SQUID magnetometer (MPMS XL7 Quantum Design). All measurements were performed in the 2 K−400 K temperature range and magnetic field up to μ$_0$H = 7 T. In higher temperature range (300 K-1050 K) the DC measurements were performed by making use of the Faraday type magnetic balance. The XPS measurements were performed with the use of PHI 5700/660 Physical Electronics spectrometer. The spectra were analyzed at room temperature using monochromatized Al K$_\alpha$ radiation (1486.6 eV). The samples were fractured and measured in vacuum of 10^{-10} Torr.

3. Results

3.1. Crystal structure

The crystal structure of studied compounds was examined by making use of XRD method. It was shown that the Tb$_x$Gd$_{1-x}$Fe$_3$ series crystallize in the rhombohedral PuNi$_3$ type of crystal structure. This type of structure is presented in the literature as equivalent to hexagonal where $a = b \neq c$ and $\alpha = \beta = 90°$, $\gamma = 120°$ [1]. The rare earth atoms in the unit cell are located in two inequivalent positions: R$_I$ in 3a(0,0,0) and R$_{II}$ in 6c (0,0,z) where $z = 0.1414$. At the same time the atoms of transition metals occupy three inequivalent positions. They are located at T$_I$ at 3b(0,0,1/2), T$_{II}$ at 6c(0,0,z) where $z = 1/3$ and T$_{III}$ at 18h (x, −x, z) where $x = 1/2$, $x = 0.0829$. Each of them has the same coordination number, but a different number of R and T atoms in different positions as the nearest neighbors.

The crystal structure parameters of the Tb$_x$Gd$_{1-x}$Fe$_3$ series are presented in Fig.1b. All of them have been estimated with the use of
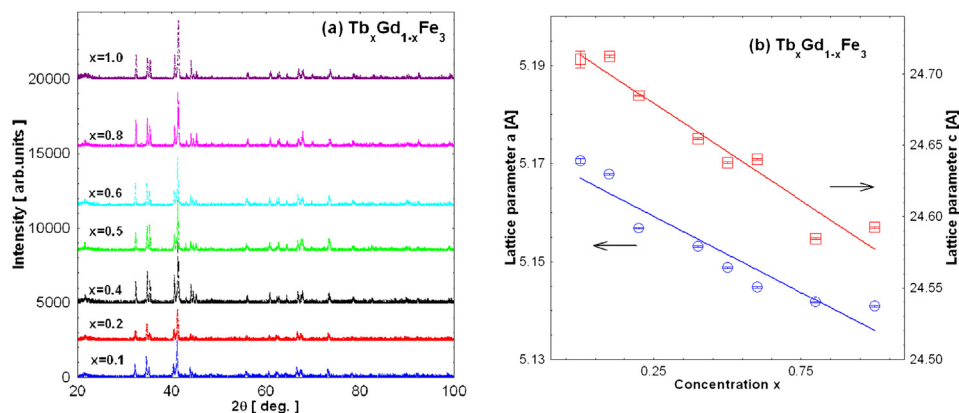

Fig. 1. XRD patterns (a); lattice parameters (b) for the Tb$_x$Gd$_{1-x}$Fe$_3$ system.