Anisotropy and FOMP in Tb$_3$ (Fe$_{28-x}$Co$_x$)$_{V_{1.0}}$ ($x=0, 3$ and $6$) compounds

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**Abstract**

In this work, the structural and magnetic properties of Tb$_3$ (Fe$_{28-x}$Co$_x$)$_{V_{1.0}}$ ($x=0, 3, 6$) compounds have been investigated. The structural characterization of compounds by X-ray powder diffraction is an evidence for a monoclinic Nd$_2$(Fe, Ti)$_{29}$-type structure ($A2/m$ space group). The refined lattice parameters $a$ and $b$ (but not $c$) and the unit cell volume $V$, obtained from the XRD data by the Rietveld method, are found to decrease with increasing $x$ concentration. The unit cell parameters behavior has been attributed to the smaller Co atoms and a preferential substitution of Fe by Co. The anisotropy field ($H_a$) as well as critical field ($H_{cr}$) was measured using the singular point detection (SPD) technique from $5$ to $300$ K in a pulsed magnetic field of up to $30$ T. At $T=5$ K, a FOMP of type $2$ was observed for all samples and persists at all temperatures up to $300$ K. For sample $x=0$, $H_{cr}=10.6$ and $2.0$ T at $5$ and $300$ K, respectively, is equal to that reported earlier. The occurrence of canting angles between the magnetic sublattices during the magnetization process instead of high-order anisotropy contributions (at room temperature are usually negligible) has been considered to explain the survival of the FOMP at room temperature. The anisotropy and critical fields behave differently for samples with $x=3$ compared with $x=6$. The observed behavior has been related to the fact that the Co substitution for Fe takes place with a preferential entrance in the inequivalent crystallographic sites of the 3:29 structure. The contribution of the Tb-sublattice in the Tb$_3$(Fe, V)$_{29}$ compound with uniaxial anisotropy has been scaled from the anisotropy field measured on a Y$_3$(Fe, V)$_{29}$ single crystal with easy plane anisotropy.

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1. Introduction

Intermetallic compounds R$_3$(Fe, M)$_{29}$ (R is a rare earth element or Y, and M—a stabilizing element such as Ti, V, Cr, Mo, etc) and their interstitial compounds have attracted considerable attention because some of them, like Sm$_3$(Fe, M)$_{29}$N$_y$, exhibit excellent hard-magnetic properties [1]. The 3:29 compounds crystallize in a monoclinic system with $A2/m$ space group and consist of tetragonal ThMn$_{12}$-type (1:12) and rhombohedral Th$_2$Ni$_{17}$-type (2:17 K) segments in a ratio of 1:1 [2]. There are two formula units and 64 atoms per unit cell such that the rare earth ions occupy two nonequivalent crystallographic sites (2a and 4i), and the Fe atoms occupy 11 sites (one 2c, one 4e, one 4g, four 4i and four 8j) [3].

Since Co has different electronic structure than Fe, and therefore a different local anisotropy, the structural and magnetic properties of 3:29 compounds are strongly affected by the partial substitution of Fe by Co atoms. In replacing Fe by small amount of Co (Cu, Ni) atoms, they substitute preferentially at Fe$_1$ (2c), Fe$_8$ (8j) and Fe$_{14}$ (4e) sites, where the Fe atoms couple with a negative exchange interaction with their neighbor atoms. The substitution of Co increases the net exchange by reducing the negative contribution of antiferromagnetically coupled sites on the 3d-sublattice and thereby fast increase of $T_C$ [4-5]. The Ti, Mo and V atoms substitute in Fe$_2$(4i), Fe$_5$(4i) and Fe$_6$(4g) sites where the dumb-bell Fe atoms are arranged in a direction close to the c-axis, while Co atoms strongly avoid these sites [4,6]. However, for large concentrations of Co atoms they occupy the dumb-bell positions [7]. For more than 40% Co substitution, when the amount of the stabilizing atom is low, a disordered modification of the hexagonal Th$_2$Ni$_{17}$-type structure is formed. It is commonly believed that the 3:29 structure will exist only for light rare earth elements [8]. For heavy rare earth beyond the Tb element, a different type of structure may be expected [9]. However, for the formation of the 3:29 phase in R$_3$(Fe$_{1-x}$Co$_x$)$_{29}$-M$_y$ system with more than 40% substituted Co atoms, a large amount of stabilizing element is needed. For example, in the case of R=Gd,
M=Cr, x=0–1, y=4–7 [10] and for R=Sm, M=Cr, x=0.4–1.0, y=4.5–7.0 [11] are found, the favored change from planar to uniaxial anisotropy has also been observed.

The magnetocrystalline anisotropy in the $Y_3(Fe, M)_{29}\text{ compounds}$ is due to the iron sublattice. X-ray powder diffraction patterns of magnetically aligned powder samples of the $Y_3(Fe,V)_{29}$ compound indicate that the magnetocrystalline anisotropy is of easy plane type [12]. The $Y_3(Fe_{1-x}Co_{x})_{29}V_{1.5}$ ($x=0.1–0.4$) compounds have also the same kind of anisotropy, but as the cobalt content increases the easy magnetization direction (EMD) that gradually turns without bending to the outside of the basal plane [13].

A uniaxial anisotropy favorable for permanent magnet applications is expected to occur in the $3:29$ system in $[20–1], [012]$ and $[010]$ directions [14]. The EMD determined experimentally for $Nd_3(Fe, V)_{29}$ [15], $Pr_3(Fe, Ti)_{29}$ [16] and $Tb_3(Fe, V)_{29}$ [8] compounds at room temperature is $[010]$ direction. For elements with $\gamma_C<0$ (Pr, Nd, Tb and Dy), the magnetocrystalline anisotropy of the rare earth sublattice in the $R_3(Fe, M)_{29}$ compounds are predicted to be uniaxial with EMD along the $[010]$ direction [12]. Since the anisotropy of the 3d-sublattice is planar, therefore the 4f anisotropy overcomes the 3d-anisotropy at room temperature. The XRD patterns of magnetically aligned powder of $Tb_3(Fe_{1-x}Co_{x})_{29}V_{1.6}$ ($x=0, 0.1$) compounds reveal the EMD to be along the b-axis ($[010]$ direction) of the monoclinic structure, but for $x=0.2, 0.3$ and 0.4 the EMD turns away from it and a tilted magnetic structures are formed [8].

A spin reorientation transition at 160 K is reported in $Tb_3(Fe_{1-x}V_{1.2})_{29}$ compound [3] but this results has been failed to be observed by magnetization measurements along the hard axis of a $Tb_3(Fe_{1-x}V_{1.2})_{29}$ single crystal [17]. A first-order magnetization process (FOMP) has been observed to occur in a $Tb_3(Fe_{1-x}V_{1.2})_{29}$ single crystal in the temperature range between 5 and 200 K [17]. In $Tb_3(Fe_{1-x}Co_{x})_{27}V_{1.6}$ ($x=0.0–0.4$) series the spin reorientation phenomena is observed in $x=0.1–0.3$ in which by increasing the Co content the transition temperature decreases from 473 K for $x=0.1$ to 393 K for $x=0.3$, and disappears in the case of $x=0.4$ [8]. In this work we have studied the effect of Co substitution on the structural and magnetic properties of $Tb_3(Fe_{28-x}Co_{x})_{V1.0}$ ($x=0, 3$ and 6) compounds.

2. Experimental

$Tb_3(Fe_{28-x}Co_{x})_{V1.0}$ ($x=0, 3, 6$) compounds were prepared by arc melting of high-purity (at least 99.9%) of the constituent elements in a water-cooled copper boat. The ingots were subsequently annealed in sealed quartz tubes under protective argon atmosphere at 1323 K for a period of 7 days in order to maximize the amount of $R_3Fe_{28-x}M_{x}$ phase then followed by quenching in water. The phase purity of the prepared samples were examined by X-ray diffraction analysis that was performed at room temperature using CuKα radiation with $2\theta=0.02^\circ$ resolution. The XRD data were analyzed using commercial TOPAS package and Fullprof program. The singular point detection (SPD) technique, with high pulsed field up to 30 T, was used to measure the temperature dependence of the anisotropy field (i.e. the magnetic field needed to rotate the magnetization vector from an easy to a hard direction) from 5 to 300 K. The SPD technique allows a precise determination of the anisotropy field even in polycrystalline samples [18]. This method is based on the assumption that if the hard axis is in the basal plane a singularity appears in the second derivative of the magnetization ($d^2M/dH^2$) exactly where the internal field reaches the anisotropy field [19]. It is worth recalling that the presence of the secondary phases does not affect the anisotropy fields determined by SPD technique.

3. Results and discussion

The XRD patterns for the annealed $Tb_3(Fe_{28-x}Co_{x})_{V1.0}$ ($x=0, 3$ and 6) compounds are shown in Fig. 1. The diffraction patterns of the main phase can be quite well indexed in the monoclinic $Nd_3(Fe, Ti)_{29}$-type structure with the space group $A2/m$. The indices $(h k l)$ of main $3:29$ phase for $x=6$ are written above the peaks.
The phase composition and unit cell parameters of the monoclinic Tb3(Fe28−xCox)V1.0 (x = 0, 3, 6) compounds; space group A2/m.

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<th>b (Å)</th>
<th>c (Å)</th>
<th>β (deg)</th>
<th>V (Å³)</th>
<th>Crystal size (nm)</th>
<th>Crystal density (g/cm³)</th>
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<td>1.49</td>
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</tbody>
</table>

Table 1. The phase composition and unit cell parameters of the monoclinic Tb3(Fe28−xCox)V1.0 (x = 0, 3, 6) compounds; space group A2/m.

Results of the Rietveld analysis using both the TOPAS package and Fullprof program indicate that there are some amounts of 1:12 (S. G. I4/mmm), and x-Fe (S. G. Im3m) phases in the samples. The strongest impurity peaks of 1:12 (2θ = 43.64° for x = 0, 3), and x-Fe (2θ = 44.65° for all samples and 2θ = 64.80° for x = 3) are marked on X-ray diffraction patterns of Fig. 1. The intensity of the peak at ~28.5° strongly depends on the composition although the peak belongs to the main 3:29 phase. Phase composition and unit cell parameters of the monoclinic Tb3(Fe28−xCox)V1.0 (x = 0, 3, 6) are shown in Table 1. The fact that free Fe atoms as well as other impurity phases found may cause a variation of the actual Fe or Co concentrations in the samples. The lattice parameters a and b (but not c) and the unit cell volume V of the compounds are decreased with increasing Co concentration due to the fact that the Fe atoms are replaced by the smaller Co atoms (Fig. 2).

The temperature dependence of the anisotropy field (Ht) of Tb3(Fe28−xCox)V1.0 (x = 0, 3, 6), as well as the critical field (Hc2) of the first-order magnetization process (FOMP) are shown in Fig. 3a and b. For these systems, it was difficult to determine the peak in the second time derivative of magnetization versus field, d²M/dt² = H, by the SPD technique. Two singularities in each isotherm SPD signal plots (d²M/dt² versus H) measured on the spinning samples in a pulsed magnetic field applied parallel to the HMD axis are observed. The first peak at a lower internal field in the SPD signals corresponds to a FOMP reflecting a magnetic-field-induced phase transition from one local minimum of the total energy (anisotropic + magnetic field energy) to another one at higher fields. As shown in Fig. 3b in all three compounds, the FOMP persists at all temperatures from 5 up to 300 K. At T = 5 K, a FOMP of type 2, in which the magnetization is not saturated after the jump, occurs in Tb3(Fe28−xCox)V1.0 (x = 0, 3) compounds at Hcr = 10.7, 8.6 and 7.0 T, respectively. According to previous reports, the FOMP transition observed in the Tb3(Fe, M)29 compounds is of type 2 [2,3,17,21–23]. Courtney et al. [17] have reported a large critical field Ht of 10.6 T at 5 K for a Tb3.5Fe44.6V6.5 (3:29 ratio) single crystal that anisotropic + magnetic field energy process (FOMP) occurs in this compound up to T = 200 K. The Hc2 at 5 K for x = 0 is equal to that reported in ref. [17]. The type-II FOMP in the magnetization of Tb3(Fe28−xCox)V1.0 (Hc2 = 2.3 T at 300 K) [23], Tb3Fe6.0Cr3.0Co24 (3:29 ratio) (Hc2 = 6.0, 5.5 T at 100 and 200 K, respectively) [23], Tb3Fe28.0Ti1.0 (Hc2 = 11.5, 8.2 T at 77 and 230 K, respectively) [21] and Tb3Fe28.0V1.0 (Hc2 = 2.0 T at 300 K) [3,22] has been reported earlier. The Hcr = 2.0 T at 300 K for x = 0 is equal to that reported earlier [3,22]. The low symmetry of the R3(Fe−M)29 structure implies that there are one easy and two hard directions. Anisotropy field is magnetic field needed to rotate the magnetization vector from an easy to a hard direction.

Therefore, two anisotropy fields Hs and Hf (Hs > Hf) are detected by the SPD method. For Tb3(Fe, V)29, the EMD is parallel to the b-axis ([0 1 0] direction of monoclinic structure), and the hard directions are along the c ([2 0 −1] direction of monoclinic structure) and a ([1 0 2] direction of monoclinic structure) axes; the latter is the hard magnetization direction of the compound at all the investigated temperatures [8,17]. However, in R3(Fe, M)29 compounds with M = V, Hs was not observed because of the occurrence of multi-fold twinning in the crystal [24]. The second peak appeared at the higher internal field in the SPD signal plot is corresponding to the anisotropy field Hs, in which the magnetization achieves the a-axis direction. The Hs = 4.2 T at 300 K for x = 0 is equal to that reported earlier [3,22].

The Tb-sublattice magnetic contribution (magnetization and anisotropy) is essential for the development of the FOMP transition in the Tb3(Fe, V)29 compound that were not observed in Y3(Fe, V)29.
compound. The survival of the FOMP even above room temperature is a striking result. The high-order anisotropy contributions are required to justify the presence of a FOMP but at room temperature are usually negligible. The occurrence of canting angles between the magnetic sublattices during the magnetization process has been considered to explain first-order magnetization processes, in Pr$_2$Co$_{17}$-type compounds [25]. Indeed, it was shown that the occurrence of canting angles in a two-sublattice system during the magnetization process is phenomenological equivalent to the presence of high-order anisotropy constants [25]. A phenomenological expression of the magnetocrystalline anisotropy for the monoclinic 3:29 structure has been derived [26], indicating a more complex expression of the magnetocrystalline anisotropy for the monoclinic compounds. The magnetocrystalline anisotropy appears to be characterized by a non-monotonous behavior with composition, as shown in Fig. 3a. The 3d-sublattice composition (Fe–Co) affects the Tb contribution to the magnetocrystalline anisotropy. At high measured temperatures the highest value of the anisotropy field is for $x=0$, 3 and 6) compounds. For Tb$_3$(Fe, Co)$_{29}$, the EMD is parallel to the $b$-axis, and the hard directions are along the $c$ and the $a$ axes; the latter is the hardest direction [8,17]. Therefore, the observed FOMP can be understood as follows: when the internal field $H$ is parallel to the HMD of the samples, the magnetic moments of Tb$_3$(Fe$_{28-3x}$,Co$_x$)$_{1.0}$ compounds might at first turn to the $c$-axis and then turn to the $a$-axis, which is the hardest direction for these compounds.

Remarkable in the measurement of the critical and anisotropy fields of the Tb$_3$(Fe$_{1-x}$Co$_x$)$_{29}$V$_{1.6}$ compounds is a change in the slope of $H_{cr}$ and $H_a$ curves versus temperature (Fig. 3a and b). This is due to the different contributions of the Tb and Fe-Co sublattices to the anisotropy field at different temperatures. The results obtained on a Y$_3$(Fe, V)$_{29}$ single crystal provide a basis for analyses of the magnetocrystalline anisotropy of rare earth (RE) compounds with magnetic rare earth atoms. The contribution of the Tb-sublattice in the Tb$_3$(Fe, V)$_{29}$ compound (with a Nd$_3$(Fe, Ti)$_{29}$-type structure) with uniaxial anisotropy can be scaled from the anisotropy field measured on a Y$_3$(Fe, V)$_{29}$ single crystal (with a CaCu$_5$-type structure) with easy plane anisotropy in polycrystalline samples. The magnetocrystalline anisotropy appears to be characterized by a non-monotonous behavior with composition, as shown in Fig. 3a. The 3d-sublattice composition (Fe–Co) affects the Tb contribution to the magnetocrystalline anisotropy. At high measured temperatures, the highest value of the anisotropy field is for $x=6$ sample. The observed behavior can be related to the fact that the Co substitution for Fe does not take place randomly but rather with a preferential entrance in the inequivalent crystallographic sites of the 3:29 structure for which there are different contributions to the anisotropy (even of opposite sign). In addition, the magnetic structure of these compounds changes by the preferential Co substitution [8] and then turn to the $a$-axis, which is the hardest direction for these compounds.

Remarkable in the measurement of the critical and anisotropy fields of the Tb$_3$(Fe$_{1-x}$Co$_x$)$_{29}$V$_{1.6}$ compounds is a change in the slope of $H_{cr}$ and $H_a$ curves versus temperature (Fig. 3a and b). This is due to the different contributions of the Tb and Fe-Co sublattices to the anisotropy field at different temperatures. The results obtained on a Y$_3$(Fe, V)$_{29}$ single crystal provide a basis for analyses of the magnetocrystalline anisotropy of rare earth (RE) compounds with magnetic rare earth atoms. The contribution of the Tb-sublattice in the Tb$_3$(Fe, V)$_{29}$ compound (with a Nd$_3$(Fe, Ti)$_{29}$-type structure) with uniaxial anisotropy can be scaled from the anisotropy field measured on a Y$_3$(Fe, V)$_{29}$ single crystal (with a CaCu$_5$-type structure) with easy plane anisotropy in polycrystalline samples. The magnetocrystalline anisotropy appears to be characterized by a non-monotonous behavior with composition, as shown in Fig. 3a. The 3d-sublattice composition (Fe–Co) affects the Tb contribution to the magnetocrystalline anisotropy. At high measured temperatures, the highest value of the anisotropy field is for $x=6$ sample. The observed behavior can be related to the fact that the Co substitution for Fe does not take place randomly but rather with a preferential entrance in the inequivalent crystallographic sites of the 3:29 structure for which there are different contributions to the anisotropy (even of opposite sign). In addition, the magnetic structure of these compounds changes by the preferential Co substitution [8]. These behaviors are also in agreement with the decreasing spin reorientation transition temperatures in the compounds [8]. The variations in anisotropy fields of the samples with turning EMD were also reported in other compounds [14,27,29] that attributed the change of anisotropy to a preferential Co substitution in these compounds.

Fig. 3. The temperature dependence of the anisotropy and critical fields of Tb$_3$(Fe$_{28-3x}$,Co$_x$)$_{1.0}$ compounds.

Fig. 4. Anisotropy field of the Tb$_3$(Fe, V)$_{29}$ compound is compared with that of Y$_3$(Fe, V)$_{29}$ single crystal [28]. The value of the anisotropy field of the Tb$_3$(Fe, V)$_{29}$ compound at 5 K is taken from Ref. [3].

4. Conclusion

In summary, samples of Tb$_3$(Fe$_{28-3x}$,Co$_x$)$_{1.0}$ compounds were prepared using arc melting of high-purity of the
constituent elements and subsequent annealing at 1323 K for a period of 1 week. The X-ray diffraction was performed using CuKα radiation with 0.02° resolution. The XRD patterns were refined by a Rietveld analysis using both the TOPAS package and Fullprof program, from which the phase purity as well as the mean crystal size was checked. In addition to the main phase, some amount of α-Fe was found. The lattice parameters α and b (but not c) and the unit cell volume V of the compounds are decreased with increasing Co concentration due to the fact that the Fe atoms are replaced by the smaller Co atoms. The unexpected c parameter behavior has been attributed to a possible preferential substitution of Fe by Co. The temperature dependence of the anisotropy field \( H_a \) as well as critical field \( (H_c) \) was measured using the SPD technique. Two singularities in each isotherm SPD signal plots \( (d^2M/dt^2 \text{ versus } H) \) measured on the spinning samples in a pulsed magnetic field applied parallel to the HMD axis are observed. The first peak at a lower internal field \( H_{cr} \) as applied parallel to the HMD of the samples, the corresponding to the anisotropy field \( H_{a} \), in which the magnetization achieves the α-axis direction. \( H_{cr}(T) \) increases with the decreasing temperature, similar to \( H_a(T) \). At \( T = 5 \text{ K} \), a FOMP of type 2 has been observed for the samples and persists at all temperatures up to 300 K. For sample \( x = 0.1 \), \( H_{cr} \) equals to 10.6, 2.0 T at 5 and 300 K, respectively, are equal to that reported earlier. The survival of the FOMP even above room temperature is a striking result. The high-order anisotropy contributions are required to justify the presence of a FOMP but at room temperature are usually negligible. The occurrence of canted angles between the magnetic sublattices during the magnetization process has been considered to explain first-order magnetization processes. Therefore, the observed FOMP can be realized as follows: when the internal field \( H \) is applied parallel to the HMD of the samples, the magnetization might first turn to the c-axis and then to the α-axis, which is the hardest direction of these compounds. The anisotropy and critical fields behave differently for samples with \( x = 0.3 \), compared with \( x = 0.6 \). The observed behavior has been related to the fact that the Co substitution for Fe takes place with a preferential entrance in the inequivalent crystallographic sites of the 3:29 structure. The contribution of the Tb-sublattice in the Tb\( _2(\text{Fe}, V)_{29} \) compound with uniaxial anisotropy has been scaled from the anisotropy field measured on a \( Y_x(\text{Fe}, V)_{29} \) single crystal with easy plane anisotropy.

References