Structural and magnetic properties of $R(Fe_{1-y}Co_y)_{12-x}Nb_x$ compounds

J. L. Wang, a) N. Tang, Y. P. Shen, D. Yang, B. Fuquan, G. H. Wu, and F. M. Yang
State Key Laboratory of Magnetism, Institute of Physics, Chinese Academy of Sciences, P.O. Box 603, Beijing 100080, People’s Republic of China

F. R. de Boer, E. Brück, and K. H. J. Buschow
Van der Waals-Zeeman Instituut, Universiteit van Amsterdam, 1018 XE Amsterdam, The Netherlands

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The magnetic properties of $RFe_{12-x}Nb_x$ and $R(Fe_{1-y}Co_y)_{11.3}Nb_{0.7}$ compounds with $R=Y$, Tb, and Dy have been investigated in the concentration region defined by $0.6<x<0.8$ and $y<0.3$, where the compounds are single phase with the ThMn$_{12}$-type of structure. The Curie temperature $T_C$ of the $RFe_{12-x}Nb_x$ compounds is almost independent of the Nb content whereas the saturation magnetization $M_s$ decreases with increasing Nb content. The spin-reorientation temperature $T_{sr}$ of the TbFe$_{12-x}Nb_x$ and DyFe$_{12-x}Nb_x$ compounds decreases monotonically with increasing $x$. Substitution of Co for Fe in $RFe_{11.3}Nb_{0.7}$ leads to a remarkable increase of $T_C$ and the appearance of a maximum in the Co-concentration dependence of $M_s$. In contrast, $T_{sr}$ decreases monotonically with increasing Co content for both $R=$Tb and Dy. The modification of T- and R-sublattice anisotropy originating from a change of the Nb content and from substitution of Co for Fe was analyzed by combining crystalline electric field theory and the individual-site model. © 2002 American Institute of Physics. [DOI: 10.1063/1.1425441]

I. INTRODUCTION

After Nd$_2$Fe$_{14}$B was discovered to exhibit excellent permanent-magnet properties, the T-rich R–T (R=rare earth or Y, T=Fe or Co) compounds have attracted much attention. In particular, much attention is given to the investigation of the structure and the magnetic properties of the ThMn$_{12}$-type of R–T compounds. The 1:12-type of R–T compounds do not only exhibit favorable magnetic properties but also have a simple crystal structure, with only one R site (2a) and three nonequivalent T sites ($i$, $j$, and $f$). Therefore these compounds are interesting materials for the study of magnetic and crystal-field interactions. The ThMn$_{12}$ structure belongs to the CaCu$_5$ family, like the 2:17 and 3:29 structures. The $RFe_{12-x}M_i$, $RFe_{17}$, and $RFe_{29-x}M_i$ phases can be derived from the CaCu$_5$-type of structure by replacing part of the R atoms by two T and can be described by $R_{1-x}(2T)xT_5$-$RT_2$. Therefore the structural and magnetic properties of the 1:12-type compounds are to some extent related with those of the 1:5-type compounds. It is generally accepted that the anisotropy of R–T compounds is determined by the interplay of the R-sublattice and the T-sublattice contributions. In the $RT_{12-x}M_i$ compounds, the element M, which is necessary to stabilize the ThMn$_{12}$ structure, plays a critical role in the magnetic properties, in particular in the magnetocrystalline anisotropy.

Experimentally, it has been shown that the magnetocrystalline anisotropy of the T sublattice in T-rich Y–T compounds with T=Fe or Co is much larger than in metallic Co or Fe. Recent investigations also indicate that in the $R_5(FeCo)$ compounds, the contributions of the individual T sites to the anisotropy originating from Co and Fe are of opposite sign, which can be understood in the terms of a local-moment description of the Co and Fe ions. Band-structure calculations on Y($Fe_{1-y}Co_y$)$_3$ have confirmed the positive sign of the Fe anisotropy at the $3g$ site and the negative sign at the $2c$ site. In order to study further the contribution to magnetocrystalline anisotropy of the Fe and Co ions and of the stabilizing element M in the ThMn$_{12}$ type of structure, in this article a systematic study is presented of the structural and magnetic properties of $RFe_{12-x}Nb_x$ and $R(Fe_{1-y}Co_y)_{11.3}Nb_{0.7}$ compounds with $R=$Tb, Dy, and Y, with emphasis on the magnetocrystalline anisotropy.

II. EXPERIMENT

$RFe_{12-x}Nb_x$ and $R(Fe_{1-y}Co_y)_{11.3}Nb_{0.7}$ compounds with $R=$Tb, Dy, and Y were prepared with $x=0.4$ to 1.0 and $y=0$ to 1 by arc melting the constituent elements (99.9 wt % purity or better) under argon atmosphere. The temperature dependence of the magnetization was measured in a superconducting quantum interference device (SQUID) magnetometer in a field of 0.1 T in the temperature range from 5 to 300 K and in a vibrating-sample magnetometer from room temperature to above the Curie temperature. The values of the Curie temperature $T_C$ were derived from $M^2 vs T$ curves by extrapolating $M^2$ to zero. X-ray-diffraction patterns of randomly oriented powder samples were used to check the phase composition of the samples investigated. The easy magnetization direction at room temperature was determined from the x-ray-diffraction patterns of magnetically aligned powder samples. Magnetization curves were measured in the vibrating-sample magnetometer or SQUID magnetometer in fields up to 7 T. In order to determine the magnetic-anisotropy field of the compounds with easy-axis anisotropy, the fine-powdered particles were mixed with epoxy resin and cured under pressure.

a)Electronic mail: jlwang@posta.unizar.es
TABLE I. Structural and magnetic parameters of TbFe$_{12-x}$Nb$_x$ compounds. The accuracy of $a$ and $c$ is about 0.002 Å, and of $T_C$ and $T_a$ about 5 K.

<table>
<thead>
<tr>
<th>$x$</th>
<th>$a$ (Å)</th>
<th>$c$ (Å)</th>
<th>$V$ (Å$^3$)</th>
<th>$T_C$ (K)</th>
<th>$T_a$ (K)</th>
<th>$\Delta V$ (Å$^3$)</th>
</tr>
</thead>
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<tr>
<td>0.55</td>
<td>8.518</td>
<td>4.787</td>
<td>347.3</td>
<td>541</td>
<td>429</td>
<td>-23.4</td>
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<td>0.60</td>
<td>8.514</td>
<td>4.785</td>
<td>346.8</td>
<td>539</td>
<td>406</td>
<td>-19.9</td>
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<tr>
<td>0.65</td>
<td>8.522</td>
<td>4.793</td>
<td>348.1</td>
<td>537</td>
<td>390</td>
<td>-17.3</td>
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<td>0.70</td>
<td>8.528</td>
<td>4.797</td>
<td>348.7</td>
<td>541</td>
<td>365</td>
<td>-16.6</td>
</tr>
<tr>
<td>0.75</td>
<td>8.526</td>
<td>4.797</td>
<td>348.7</td>
<td>537</td>
<td>326</td>
<td>-10.9</td>
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<tr>
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<td>4.795</td>
<td>348.3</td>
<td>534</td>
<td>299</td>
<td>-9.2</td>
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</tbody>
</table>

packed in a plastic cylinder which was then placed in a field of about 1 T. The cylinder axis was kept parallel or perpendicular to the field direction to obtain the easy magnetization direction and the hard magnetization direction, respectively. For the compounds with easy-plane anisotropy, a rotation alignment technique was used to obtain the hard magnetization direction. The anisotropy fields $B_a$ at room temperature were determined by means of the singular-point-detection method. The values of $B_a$ at low temperature were derived from $\Delta M = M_\parallel - M_\perp$ vs $B$ curves by extrapolating $\Delta M$ to zero.

III. RESULTS AND DISCUSSION

A. Structure and phase constitution

Both the x-ray-diffraction patterns and the thermomagnetic curves indicate that single-phase TbFe$_{12-x}$Nb$_x$ compounds have been obtained only for $0.55 \leq x \leq 0.80$, while for $x < 0.55$ and $x > 0.8$ the 2:17 phase and $\alpha$-Fe phase appear as impurity phases. From our experimental results and the experimental data in Ref. 14, it can be concluded that the homogeneity region of the ThMn$_{12}$ phase is different for the various rare-earth elements. For R=Tb, the 1:12 phase is stable in the range of $0.55 \leq x \leq 0.8$, and for R=Dy in the range $0.6 < x < 0.8$. Table I summarizes the lattice and magnetic parameters of TbFe$_{12-x}$Nb$_x$ compounds. It can be seen that the unit-cell volume increases slightly with increasing Nb content due to the larger metallic radius of Nb (1.46 Å) compared to Fe (1.26 Å).

Table II presents the metallic radii for 12-fold coordination of the stabilizing elements M and the experimentally obtained 1:12 phase homogeneity range of RFe$_{12-x}$M$_x$ compounds with M=Tb, V, Cr, Nb, and Ta. It can be seen that, compared with other stabilizing elements such as V, Cr, Mo, etc., the homogeneity range is rather narrow for Ti, Nb, and Ta. It is probable that the size of the M atom plays an important role in the ability to stabilize the 1:12 structure. It is clear that the larger the radius the lower the content of the stabilizing element needed to stabilize the ThMn$_{12}$ type of structure. On the other hand, an excessive enhancement of the unit-cell volume due to the introduction of the stabilizing element Ti, Nb, or Ta will make the 1:12 structure unstable again, which leads to a narrower homogeneity range of RFe$_{12-x}$M$_x$ for Ti, Nb, or Ta compared with the other M elements.

The site occupation of the stabilizing element M in RFe$_{12-x}$M$_x$ compounds can be analyzed in terms of the metallic radii and the heat of mixing of the elements R and M, as has been done previously. For the Wigner–Seitz cell volumes of the 3$d$-metal sites in RFe$_{12-x}$M$_x$ compounds, one has $V(8i) > V(8j) > V(8f)$. On the basis of the average T–T distances, it can be expected that the Nb atoms prefer the 8i site to the 8f or 8j sites, which has also been proved by neutron powder-diffraction experiments.

For a fixed Nb concentration of $x=0.7$, we have prepared several R(Fe$_{1-x}$Co$_x$)$_{11.3}$Nb$_{0.7}$ compounds. From our experimental results it can be concluded that the homogeneity range of the 1:12 phase spans the y range 0–0.2 for R=Y and 0–0.3 for R=Tb and Dy. Because Co (1.25 Å) has a smaller radius than Fe (1.26 Å), one expects that the Co atoms show preference for the 8f and 8j sites over the 8i sites. The preferential occupation of Co can also be explained in the terms of enthalpy effects. Taking the Y(Fe$_{1-x}$Co$_x$)$_{11.3}$Nb$_{0.7}$ system as an example, according to the semiempirical Miedema model the values of the enthalpies of the binary alloys that reflect the interaction of Y with the various metals are found to be 139 to 102 kJ/mol for Y–Nb, −112 to −67 for Co–Y, −6 to −4 for Fe–Y, −111 to −88 for Co–Nb, −70 to −57 for Fe–Nb, and −2 for the Fe–Co system. These values suggest that Nb and Fe tend to occupy those sites for which the contact with Y is weak, while the Co atoms prefer to make as much contact as possible with the Y atoms. From the coordination around the Y atoms in the Y(Fe$_{1-x}$Co$_x$)$_{11.3}$Nb$_{0.7}$ compounds, it can be seen that only one Y atom is present in the coordination shell of the 8i sites while the 8j and 8f sites have two Y atoms in their coordination shell. This implies that there is a less strong interaction between the Y and the Co atoms when the latter atoms occupy the 8i sites. The enthalpy effects reinforce the site preference due to size effects mentioned above. These conclusions are also consistent with our experimental neutron-diffraction results on Y(Fe$_{1-x}$Co$_x$)$_{11}$Ti compounds.

B. Intrinsic magnetic properties

1. Curie temperature and exchange interaction

Figure 1 shows the concentration dependence of the Curie temperature $T_C$ of RFe$_{12-x}$Nb$_x$ compounds with R=Tb (a) and Dy (b). It can be seen that, in both systems, the values of $T_C$ are almost independent of the Nb content. In the RFe$_{12-x}$Nb$_x$ compounds, the influence of Nb on $T_C$ is simi-
lar to the case of the RFe$_{12-x}$M$_x$ compounds with M=Ti and W, but different from the RFe$_{12-x}$M$_x$ compounds with M=Al, V, Cr, M, and Mo, where $T_C$ clearly decreases with increasing M content. It is also different from the RFe$_{12-x}$Si$_x$ compounds with M=Si where, for example in the LuFe$_{12-x}$Si$_x$ compounds, $T_C$ slightly increases with increasing Si content from 528 K for $x=1.5$ to 540 K for $x=2.0$.

Figure 2 shows the concentration dependence of $T_C$ of the R(Fe$_{1-y}$Co$_y$)$_{11.3}$Nb$_{0.7}$ compounds with R=Tb (a) and Dy (b). The concentration dependence of $T_C$ of the Y(Fe$_{1-y}$Co$_y$)$_{11.3}$Nb$_{0.7}$ compounds is shown in Fig. 3. It can be seen that substitution of Co for Fe leads to a clear increase of the Curie temperature. The exchange interaction between the R and the T sublattice can be described by means of a molecular field $B_{mol}$ acting on the R ions due to the surrounding T spins. The molecular field, $B_{mol}$, can be derived from the experimentally obtained value of $T_C$ by means of the following equation

$$B_{mol} = \frac{3k_BT_C}{gJ(J+1)\mu_B}.$$  (1)

Assuming Eq. (1) to be applicable to the 3d magnetism (with $g=2$ and $J=S$) and using the experimental values of $T_C$ and the atomic magnetic moment $\mu_T$ ($S=S_T=\mu_T/2$), we have derived values for $B_{mol}$ in the Y(Fe$_{1-y}$Co$_y$)$_{11.3}$Nb$_{0.7}$ compounds. The dependence of $B_{mol}$ on the Co concentration is shown in Fig. 3. The values of $B_{mol}$ illustrate the magnitude of the internal fields present in Y(Fe$_{1-y}$Co$_y$)$_{11.3}$Nb$_{0.7}$ compounds due to the 3$d$–3$d$ interaction. It can be seen that the internal fields are clearly enhanced due to the substitution of Co for Fe.

2. Saturation magnetization

Values for the saturation magnetization at 4.2 K and at room temperature were derived from $M$ vs $1/B$ plots by extrapolating $1/B$ to zero, using the high-field data of the magnetization curves of fine-powder samples. As examples, the Nb-concentration dependencies of $M_s$ of the TbFe$_{12-x}$Nb$_x$ and DyFe$_{12-x}$Nb$_x$ compounds are shown in Figs. 4(a) and 4(b), respectively. It can be seen that $M_s$ monotonically decreases with increasing Nb content. Moreover, the decrease is much faster than expected from a simple dilution model.

FIG. 1. Concentration dependence of the Curie temperature $T_C$ and the spin-reorientation temperature $T_{sr}$ for (a) TbFe$_{12-x}$Nb$_x$ and (b) DyFe$_{12-x}$Nb$_x$ compounds.

FIG. 2. Concentration dependence of the Curie temperature $T_C$ and the spin-reorientation temperature $T_{sr}$ for (a) Tb(Fe$_{1-y}$Co$_y$)$_{11.3}$Nb$_{0.7}$ and (b) Dy(Fe$_{1-y}$Co$_y$)$_{11.3}$Nb$_{0.7}$ compounds.

FIG. 3. Composition dependence of the Curie temperature $T_C$, the molecular field $B_{mol}$, and the magnetic moment per 3$d$ atom $\mu_{3d}$ at 4.2 K in Y(Fe$_{1-y}$Co$_y$)$_{11.3}$Nb$_{0.7}$ compounds.
Both the experimental results and band calculations\textsuperscript{3} show that the average atomic magnetic moments of Fe in the 1:12 structure varies in the sequence $m_{\text{Fe}}(8i) > m_{\text{Fe}}(8j) > m_{\text{Fe}}(8f)$. The faster decrease of $M_s$ with increasing Nb content may be associated with the preferential occupancy of Nb of the $8i$ site as mentioned above.

Substitution of Co for Fe leads to the appearance of a maximum in the concentration dependence of the average atomic magnetization of the $T$ sublattice, $M_T = M_f/11.3$ in the $\text{Y(Fe}_{1-x}\text{Co}_x)_{11.3}\text{Nb}_{0.7}$ compounds, as shown in Fig. 3. It can be understood in the terms of modification of the $3d$ subband structure of the Fe atoms due to the introduction of Co as discussed for the binary Fe–Co alloys and quasi-binary or quasi-ternary $\text{R(Fe,Co)}_m\text{M}_z$ compounds.\textsuperscript{26,27}

3. Magnetocrystalline anisotropy

a. Influence of Nb on the anisotropy. Figure 5 shows the temperature dependence of the ac susceptibility $\chi$ of the DyFe$_{12-x}$Nb$_x$ compounds. Below room temperature, two peaks are seen in the $\chi$-$T$ curves. The temperature dependence of the magnetization measured in a low field also shows anomalies around the temperatures at which the anomalies occur in the $\chi$-$T$ curves. In order to examine what happens at these critical temperatures, the dependence of the magnetization $M$ on the angle $\theta$ between the alignment direction and the external field direction was measured at various temperatures. It is clear that, at a temperature where the anisotropy of the compound is either easy-axis or easy-plane type, there should be only one maximum in the $M$-$\theta$ curve between $0^\circ$ and $180^\circ$. There should be two maxima for a compound with an easy-cone anisotropy. If the easy magnetization direction changes in the temperature range investigated, the position of the maximum in the $M$-$\theta$ curves will change. As an example, we show in Fig. 6 the angular dependence of the magnetization of the compound $\text{DyFe}_{11.3}\text{Nb}_{0.7}$ at various temperatures in a field of 1.0 T. It can be seen that, if the temperature increases from 5 to 300 K, the number of maxima changes from one at 25 and 80 K, becoming two at 120, 150, and 180 K, and going back to one
at 300 K. The position of the maximum shifts from 0° at 25 K to 90° at 300 K. From this, it can be concluded that the peak or the anomaly in the M-T or χ-T curve corresponds to a spin reorientation. With increasing temperature, the easy magnetization direction of the DyFe12−xNb, compounds changes from easy plane, via an easy-cone range, to easy axis. The values of the spin-reorientation temperature $T_{sr}$ were determined from the peaks in the χ-T curves. They are in agreement with those derived from the anomalies in the M-T curves. In Figs. 1 and 2, tentative magnetic phase diagrams are presented for the RFe12−xNb, and R(Fe1−yCo,y)11.3Nb0.7 compounds, respectively.

The x-ray-diffraction patterns of magnetically aligned powder samples at room temperature show that, for the RFe12−xNb, compounds with R=Y and Dy, the easy magnetization direction is along the c axis whereas it is perpendicular to the c axis for R=Tb. In R−T compounds, the total magnetocrystalline anisotropy is determined by the interplay of T- and R-sublattice contribution. Because Y is nonmagnetic and does not contribute to the magnetocrystalline anisotropy in the YFe12−xNb, compounds, it can be concluded that the Fe-sublattice anisotropy is of easy-axis type at room temperature. Moreover, the magnetic measurements indicate that there is no spin reorientation in YFe12−xNb, so that it can be concluded that the Fe sublattice has a positive anisotropy constant $K_{Fe}^{tot}$ in the whole temperature region up to the Curie temperature.

According to crystal-field theory, the total anisotropy constant $K_{tot}^{mol}$ can in first-order approximation be expressed as

$$K_{tot}^{mol} = K_{Fe}^{mol} + K_{Fe}^{R} = K_{Fe}^{mol} - \frac{1}{2} \alpha_{J} A_{20}(O_{20}) (r^2).$$

It can be assumed that, in the series of RFe12−xNb, compounds, the crystal-field parameter $A_{20}$ is the same for all rare-earth elements at a fixed Nb content. Because $A_{20}$ in RFe12−xNb, is negative, the Tb and the Dy ion have a negative $\alpha_{J}$ value, the Tb and the Dy sublattice favor easy-plane anisotropy.

In Fig. 1(a) it can be seen that in the TbFe12−xNb, compounds the spin-reorientation temperature $T_{sr}$ decreases monotonically with increasing Nb content. This suggests that the easy-plane anisotropy of the Tb sublattice becomes further weakened compared with the easy-axis anisotropy of the Fe sublattice. It is known that Nb preferentially occupies the Fe 8i sites. Therefore one may expect that the easy-axis anisotropy resulting from the Fe sublattice will decrease with increasing Nb content. The results obtained for the TbFe12−xNb, compounds indicate that the easy-plane anisotropy of the Tb sublattice decreases much faster than the easy-axis anisotropy of the Fe sublattice. According to Eq. (2), the decrease of the easy-plane anisotropy of the Tb sublattice may be attributed to a decrease of the crystal-field parameter $A_{20}$ with increasing Nb content since $T_{C}$ of the TbFe12−xNb, compounds is almost independent of the Nb concentration. At the spin-reorientation temperature $T_{sr}$, we have

$$K_{Fe}^{R} (T_{sr}) = K_{Fe}^{R} (0) m_{R} (T)^{3} = K_{Fe}^{R} (0) B_{J}^{3}(y) = - K_{Fe}^{T} (T_{sr}),$$

where $K_{Fe}^{R}$ and $K_{Fe}^{T}$ represent the anisotropy constants per formula unit, $B_{J}(y)$ is the Brillouin function, and $m_{R}(T)$ is the magnetization of the Tb sublattice.

The calculated values of $T_{sr}$ decrease monotonically with increasing Nb content. This suggests that the Fe sublattice anisotropy is of easy-axis type at room temperature. Moreover, the magnetic measurements indicate that there is no spin reorientation in YFe12−xNb, so that it can be concluded that the Fe sublattice has a positive anisotropy constant $K_{Fe}^{tot}$ in the whole temperature region up to the Curie temperature.

For TbFe12−xNb, compounds, the values of $T_{sr}$ are near or above 300 K. This is high enough to use the high-temperature limit of the Brillouin function, as was done in a previous analysis of crystal-field effects. We have

$$T_{sr} = \frac{M_{R}(T)/M_{R}(0)}{N_T} = \frac{Z_{RT} M_{T}(g_{J} - 1) (J + 1) J_{RT}^{3}}{18 K_{Fe}^{tot}}.$$
Because in the present case the maximum Co concentration in the Y(Fe_{1-x}Co_{x})_{11/3}Nb_{0.7} compounds is limited to 0.2, a minimum of B_{s} in the concentration dependence, as found for the Y(Fe_{1-x}Co_{x})_{11/3}Ti compounds, was not observed. But, for x ≈ 0.2, the experimental results are similar to those for Y(Fe_{1-x}Co_{x})_{11/3}Ti. Because the Y atoms do not contribute to the magnetocrystalline anisotropy, the total anisotropy is only due to the 3d sublattice. The anisotropy constant $K_{1}^{T}$ of the 3d sublattice in the Y(Fe_{1-x}Co_{x})_{11/3}Nb_{0.7} compounds can be calculated by using the relation, $K_{1}^{T} = (B_{s}M_{s})/2$. The concentration dependencies of $K_{1}^{T}$ at 5 K and at room temperature are also shown in Fig. 7. It can be seen that there exists a maximum of $K_{1}^{T}$ at about x = 0.1.

It is well known that the contribution to the anisotropies of the Co atoms at the 2c and 3g sites in the 1:5 type of structure have opposite sign.\textsuperscript{10,11} The contribution of the Fe atoms at either the 2c or the 3g site is just the opposite of that of Co atoms at the corresponding sites. Similarly, in the 2:17 structures, except for the 6g (or 9d) site, at the other three sites the individual contributions from Co and Fe also have opposite sign.\textsuperscript{10} Using the site-transformation matrix, the site-corresponding relations between the 1:12 and 1:5 as well as between the 1:12 and 2:17H structures were obtained, as listed in Table III. It can be seen that one-half of the 8i sites corresponds to the 2c site and the other half originates from the R site. The 8f sites correspond to the 3g sites whereas the 8j sites are related to both the 2c and the 3g sites. Therefore it can be expected that the contribution of the 8i site to the anisotropy will be related to that of the 2c site while the contribution of the 8f site will be of a sign opposite to the contribution of the 8i site.

The different contributions to the magnetocrystalline anisotropy resulting from the corresponding sites in the 1:12 and 1:5 type of structures can be understood from the transformation relation of the principal axis in these two structures. Table IV lists the relations between the main reflection peaks in the different type structures obtained by means of the transformation matrices\textsuperscript{4} between the 1:5 and 1:12, and between the 1:5 and 2:17 structures. It can be seen that the c axis of the 1:12 structure lies in the ab-plane of the 1:5 structure while the c axis of the 2:17 structure is parallel to the c axis of the 1:5 structure. Taking the Fe-based compound as an example, it has been found\textsuperscript{10} that the Fe atoms at the 2c site in the compound YFe_{x} have a very strong contribution to easy-plane anisotropy ($K_{1}^{Fe} = -311.4$ K/Fe) while the Fe atoms at the 3g site exhibit a weak easy-axis anisotropy ($K_{1}^{Fe} = 66.75$ K/Fe). Therefore one expects that the Fe atoms at the 8i sites of the 1:12 structure will have a larger contribution to the easy-axis anisotropy. The contribution of the Co sublattice to the anisotropy is just the opposite.

From the neutron-diffraction investigation on Y(FeCo,Ti)$_{12}$ compounds, it is known that Co has a strong preference for the 8f and 8j sites while Fe prefers the 8i sites. Therefore the appearance of the maximum in the Co concentration dependence of $B_{s}$ and $K_{1}^{T}$ may be associated with the preferential occupation of the Co atoms.

From the concentration dependence of $T_{xw}$ of the Tb(Fe_{1-x}Co_{x})_{11/3}Nb_{0.7} compounds shown in Fig. 2(a), it can be seen that $T_{xw}$ decreases monotonically with increasing Co content, which indicates that, in a certain temperature region, the anisotropy constant $K_{1}^{tot}$ increases with increasing x. Within the picture of a simple two-sublattice model, the total anisotropy $K_{1}^{tot}(x)$ of the Tb(Fe_{1-x}Co_{x})_{11/3}Nb_{0.7} compounds can be expressed by $K_{1}^{tot}(x) = K_{1}^{Fe}(x) + K_{1}^{Co}(x)$. In first-order approximation, using the same method as described in the previous section, the $A_{20}$ values for Tb(Fe_{1-x}Co_{x})_{11/3}Nb_{0.7} were calculated from the experimental values of $T_{xw}$ listed in Table V. It can be seen that with increasing Co concentration the absolute value of $A_{20}$ decreases. As reported earlier, in the RT$_{12-x}$M$_{x}$ compounds with the ThMn$_{12}$ type of structure, when T changes from Fe to Co, $A_{20}$ changes its sign.

| TABLE III. Relations between the T sites in the 1:5, 1:12, and 2:17 structure types. |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| 1:12            | 1:5             | 2:17H*          | 1:5             |
| 8f              | ← 3g            | 4f              | ← $R^{*}(1a)$   |
| 8j(1/2)         | ← 2c            | 12j             | ← 3g            |
| 8j(1/2)         | ← 3g            | 6g              | ← 3g            |
| 8i(1/2)         | ← 2c            | 12j             | ← 2c            |
| 8i(1/2)         | ← 2c            | 18f             | ← 2c            |

$^{a}2:17R^{*}$: Rhombohedral structure of 2:17 compounds.

$^{b}2:17H^{*}$: Hexagonal structure of 2:17 compounds.

$^{c}R^{*}(1a)$: Rare-earth site of the 1:5 structure.

| TABLE IV. Relations between the reflections in different types of structures. |
|-----------------|-----------------|-----------------|-----------------|
| 1:5             | 2:17R           | 2:17H           | 1:12T           |
| 100             | 120             | -110            | 101             |
| 110             | 1-10            | -110            | 1001            |
| 120             | 100             | -540            | 103             |
| 1-10            | 110             | 110             | 100             |
| 001             | 001             | 001             | 010             |

| TABLE V. Structural and magnetic parameters of Tb(Fe_{1-x}Co_{x})_{11/3}Nb_{0.7} compounds. Accuracy of a and c: ±0.002 Å, of $T_{C}$ and $T_{xw}$: ±5 K. |
|-----------------|-----------------|-----------------|-----------------|
| x               | a (Å)           | c (Å)           | $V$ (Å$^{3}$)   | $T_{C}$ (K)   | $T_{xw}$ (K) | EMD        | $A_{20}$ (K$\alpha^{2}$) |
| 0.00            | 8.528           | 4.797           | 348.7           | 541           | 365          | planar     | -16.6      |
| 0.05            | 8.524           | 4.791           | 348.1           | 615           | 331          | planar     | -16.5      |
| 0.10            | 8.523           | 4.786           | 347.7           | 666           | 328          | planar     | -14.8      |
| 0.15            | 8.520           | 4.784           | 347.2           | 712           | 306          | planar     | -10.2      |
| 0.20            | 8.516           | 4.784           | 346.9           | 761           | 268          | uniaxial   | -6.5       |
| 0.30            | 8.505           | 4.780           | 345.7           | 821           | 247          | uniaxial   | -5.1       |
from negative to positive. This means that substitution of Co for Fe leads to a decrease of the absolute value of $A_{20}$ for small Co concentrations. The calculated values of $A_{20}$ listed in Table V are consistent with this finding.

For the Dy(Fe$_{1-x}$Co$_x$)$_{11.3}$Nb$_{0.7}$ compounds it can be seen from Fig. 2(b) that $T_{s1}$ decreases monotonically with increasing Co content, while $T_{s2}$ is almost independent of the Co content. In order to understand the concentration dependence of $T_{s1}$ and $T_{s2}$, one has to take into account higher-order crystal-field terms, at least up to fourth order.

IV. CONCLUSIONS

Single-phase RFe$_{12-x}$Nb$_x$ compounds with R=Tb and Dy having the ThMn$_{12}$-type of structure were synthesized in a narrow range of about $x = 0.6 - 0.8$. The spin-reorientation temperature $T_{sr}$ of both the TbFe$_{12-x}$Nb$_x$ and the DyFe$_{12-x}$Nb$_x$ compounds decreases monotonically with increasing $x$, while the Curie temperature $T_C$ is almost independent of the Nb content. The second-order crystal-field parameter $A_{20}$ for the TbFe$_{12-x}$Nb$_x$ compounds has been derived from the concentration dependence of $T_{sr}$. It is worthy to note that $A_{20}$ increases rapidly with increasing Nb content from $-23.4 K a_0^2$ for $x = 0.55$ to $-9.2 K a_0^2$ for $x = 0.8$, which leads to a decrease of the Tb-sublattice anisotropy which is much faster than that of the Fe-sublattice anisotropy. The decrease of the saturation magnetization $M_s$ with increasing Nb content is faster than expected in the case of simple dilution.

The maximum substitution of Co for Fe in RFe$_{11.3}$Nb$_{0.7}$ compounds is limited to 20 at. % for R=Y and to 30 at. % for R=Tb and Dy. Substitution of Co for Fe leads to a remarkable increase of $T_{sr}$ and the appearance of a maximum in the composition dependence of the saturation magnetization $M_s$. The spin-reorientation temperature $T_{sr}$ of Tb(Fe$_{1-x}$Co$_x$)$_{11.3}$Nb$_{0.7}$ compounds decreases monotonically with increasing Co content. The crystal-field parameters $A_{20}$ for the Tb(Fe$_{1-y}$Co$_y$)$_{11.3}$Nb$_{0.7}$ compounds have been derived from the Co-concentration dependence of $T_{sr}$. It is noteworthy that substitution of Co for Fe leads to a shift of $A_{20}$ from negative to positive. For Dy(Fe$_{1-x}$Co$_x$)$_{11.3}$Nb$_{0.7}$ compounds, $T_{s1}$ decreases monotonically with increasing Co content, while $T_{s2}$ is almost independent of the Co content.

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