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Structural and magnetic properties of R(Fe, Ni)$_{11.3}$Nb$_{0.7}$ compounds with R = Dy and Er

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Abstract. The effect of the substitution of Ni for Fe on the magnetic and structural properties of RFe$_{11.3}$Nb$_{0.7}$ compounds (R = Dy and Er) has been studied. All of the compounds studied crystallize in the ThMn$_{12}$ type of structure and the lattice constants a and c decrease with increasing Ni content. Substitution of Ni for Fe leads to a clear increase of the Curie temperature and to a decrease of the saturation magnetization. The temperature dependencies of the ac susceptibility and the magnetization indicate spin reorientations in all of the compounds. The easy-magnetization direction at room temperature has been determined to be along the c-axis from x-ray diffraction patterns of magnetically aligned samples. The effect of Ni substitution on the magnetocrystalline anisotropy is also discussed.

1. Introduction

Since the excellent permanent-magnet performance of Nd$_2$Fe$_{14}$B was first reported [1], the study of rare-earth–transition-metal (R–T) compounds has been intensified worldwide. Recently, Sm$_3$(Fe, Ti)$_{29}$N$_y$ compounds have been found to possess uniaxial anisotropy, hence becoming novel candidates for permanent-magnet materials [2]. Some emphasis has been placed on intermetallic compounds of the ThMn$_{12}$ structure. The ThMn$_{12}$ structure is a body-centred tetragonal one (space group $I4/mmm$) with one single R site (2a) and three T sites (8i, 8j, 8f). It is a simple structure derivative of the basic SmCo$_5$ structure type, where the former is obtained by replacing some of the rare-earth atoms by dumb-bell pairs of transition-metal atoms. Although the pure RFe$_{12}$ compounds do not exist for any of the R elements, the ThMn$_{12}$ structure can be stabilized in pseudobinaries of the type RFe$_{12-x}$M$_x$, where M is a stabilizing element and M = Al, Ti, V, Cr, Mo, Si, etc. A systematic investigation [3] of R(T, M)$_{12}$ (T = Fe, Co) compounds has indicated that the element M not only plays an important role in stabilizing the structure and in deciding the value of the Curie temperature, but also has an influence on the magnetic anisotropy. Recently, Hu *et al* reported [4] that ThMn$_{12}$-type compounds can also be stabilized by adding a small amount of Nb, which is favourable since reduction of the amount of stabilizing element generally leads to an increase of the magnetization. On the other hand, replacement of Fe or the R element in R–T compounds by other elements is becoming established as an effective

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method for improving the magnetic performance of a certain material and studying the physical properties of R–T compounds [5–7]. A spin-reorientation transition is characterized by a change of the easy-magnetization direction (EMD) from one crystallographic direction to another. Up to now, two kinds of spin-reorientation transition have been observed. One is caused by a temperature-induced competition between the two sublattice anisotropies which have different preferential directions. The second one results from a temperature-induced competition between different crystalline-electric-field (CEF) terms.

Earlier, we investigated the effect of the substitution of Ni for Fe on the structure and the magnetic properties of $HoFe_{11.3}Nb_{0.7}$ [8]. In the present paper, a study is reported of the influence of the substitution of Ni for Fe on the magnetic properties of $RFe_{11.3}Nb_{0.7}$ compounds with R = Er and Dy.

2. Experimental procedure

$R(Fe_{1-x}Ni_x)_{11.3}Nb_{0.7}$ compounds with x ranging from 0.0 to 0.3 were prepared by arc melting the 99.9% pure materials in a pure-argon atmosphere. An additional amount of R was added to compensate for the loss during the melting process. X-ray diffraction with Cu Kα radiation was employed to determine the phases and the lattice parameters. X-ray diffraction patterns of magnetically aligned powder samples at room temperature were used to determine the easy-magnetization direction in these compounds. The aligned samples were prepared by fixing powder particles at room temperature in a field of 1 T with epoxy resin. The temperature dependence of the magnetization ($\sigma(T)$) was measured in a low field of 0.04 T from room temperature up to 800 K and from 5 K to 350 K using a VSM and a SQUID magnetometer, respectively. The Curie temperatures T_C were determined from σ^2–T plots by extrapolating σ^2 to zero. The saturation moments were determined from magnetization curves at 5 K obtained in the SQUID magnetometer by extrapolating the saturated part of the magnetization curves to $B = 0$.

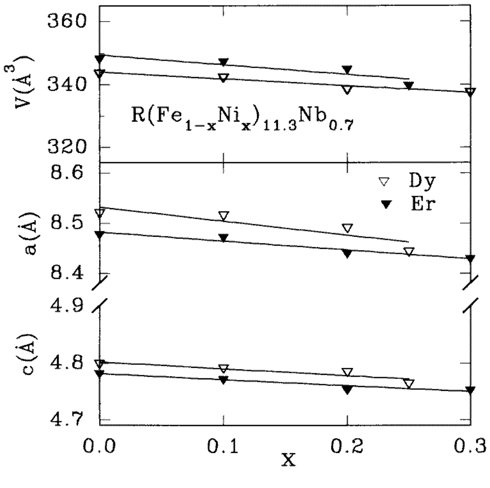

Figure 1. Lattice parameters and unit-cell volumes of $R(Fe_{1-x}Ni_x)_{11.3}Nb_{0.7}$ compounds with R = Er, Dy. The lines are guides to the eye.

Table 1. The lattice parameters a and c, unit-cell volume V, Curie temperature T_C, saturation moment M_s at 5 K and easy-magnetization direction (EMD) at room temperature (RT) of R(Fe$_{1-x}$Ni$_x$)$_{11.3}$Nb$_{0.7}$ compounds.

x	a (Å)	c (Å)	V (Å^3)	T_C (K)	M_s (μ_B/f.u.)	EMD at RT
R = Er						
0.0	8.478	4.782	343.8	498	10.6	Easy axis
0.1	8.472	4.772	342.5	563	9.7	Easy axis
0.2	8.440	4.754	338.6	618	9.1	Easy axis
0.3	8.429	4.753	337.7	643	7.8	Easy axis
R = Dy						
0.0	8.520	4.799	348.3	528	11.1	Easy axis
0.1	8.516	4.791	347.4	586	10.5	Easy axis
0.2	8.491	4.785	345.0	623	9.2	Easy axis
0.25	8.444	4.765	339.7	648	8.9	Easy axis

3. Results and discussion

The x-ray diffraction patterns show that all of the compounds investigated crystallize in the ThMn$_{12}$ type of structure except for a small amount of α-Fe present as an impurity phase. For $x > 0.3$, the x-ray diffraction patterns show the presence of another impurity phase. From figure 1 and table 1, it can be seen that the lattice parameters decrease with increasing Ni content which is due to the smaller radius of Ni compared with Fe. Figure 1 also shows that the lattice parameters of the Dy-based compounds are larger than those of the corresponding Er-based compounds, which is due to the lanthanide contraction.

The x-ray diffraction patterns of magnetically aligned samples are shown in figure 2. It can be seen that for all Er(Fe$_{1-x}$Ni$_x$)$_{11.3}$Nb$_{0.7}$ compounds the (002) reflection is enhanced and dominant with respect to other peaks, which indicates that the easy-magnetization direction is along the c-axis at room temperature. It can be concluded that, for $x \leqslant 0.3$, the substitution of Ni for Fe does not change the easy-magnetization direction. For Dy(Fe$_{1-x}$Ni$_x$)$_{11.3}$Nb$_{0.7}$, the case is similar.

From figures 3(a) and 3(b) and table 1, it can be seen that, in both of the series Er(Fe$_{1-x}$Ni$_x$)$_{11.3}$Nb$_{0.7}$ and Dy(Fe$_{1-x}$Ni$_x$)$_{11.3}$Nb$_{0.7}$, T_C increases monotonically with increasing Ni content. It is well known that there are three types of exchange interaction in RFe$_{11-x}$M$_x$ compounds, namely, the R–R interaction between the R magnetic moments, the T–T interaction between the T magnetic moments, and the R–T interaction between the R and T moments. Among these, the T–T interaction is the strongest and mainly determines the ordering temperature and the temperature dependence of the nearest T moment [9]. This interaction is very sensitive to the distance between the T moments. In RFe$_{12-x}$M$_x$ compounds, there are three crystallographically non-equivalent Fe sites which are denoted as Fe(8i), Fe(8j) and Fe(8f). Hu *et al* [4] reported that Nb occupies the 8i site and that Fe at the 8i site has the largest magnetic moment, while Fe at the 8f site has the smallest moment. The interatomic distances between the nearest neighbours of Fe atoms at the different sites are different. For the average Fe–Fe distances, the following relation holds: $d_{\mathrm{Fe-Fe}}(8i) > d_{\mathrm{Fe-Fe}}(8j) > d_{\mathrm{Fe-Fe}}(8f)$ [10]. It is well accepted [10] that in RFe$_{12-x}$M$_x$ compounds the T–T exchange interactions are positive at larger distances and negative at smaller distances. So, when the substitution of Ni for Fe occurs at sites where the distance between Fe–Fe pairs is smaller than a certain critical distance, the negative interaction

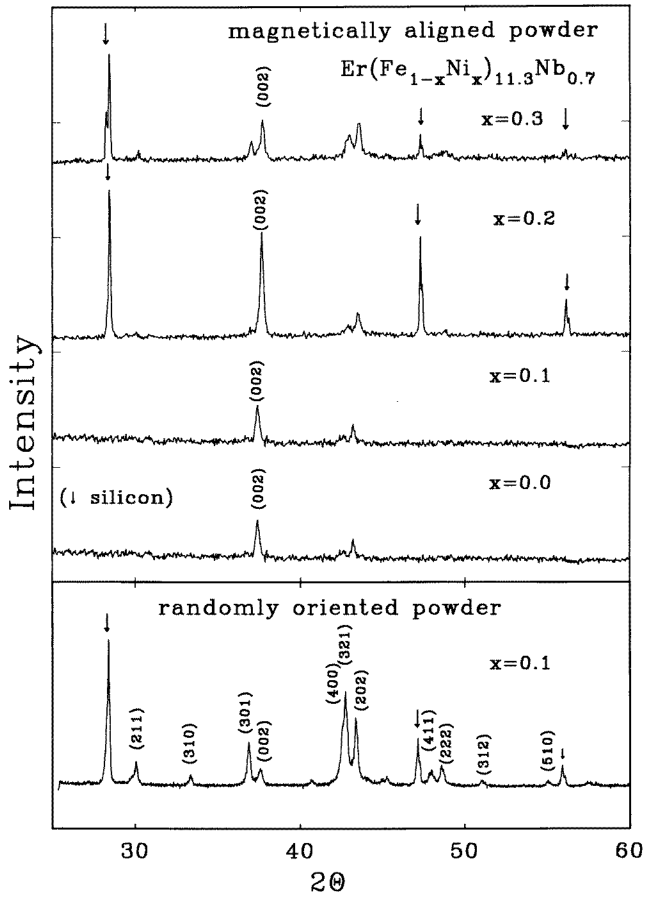

Figure 2. X-ray diffraction patterns of randomly oriented powder of Er(Fe$_{0.9}$Ni$_{0.1}$)$_{11.3}$Nb$_{0.7}$ and of magnetically aligned powder of Er(Fe$_{1-x}$Ni$_x$)$_{11.3}$Nb$_{0.7}$ compounds.

will be reduced and the total interaction will be enhanced. So, the increase of the Curie temperature due to substitution of Ni for Fe can be understood in the terms of preferential occupancy of Ni atoms at the sites with smaller Fe–Fe distances.

The saturation moments M_s have been determined from M–B curves and the values are listed in table 1. In the compounds involving a heavy R element and a late T element, the R moments are antiparallel to the T moments. If we take the moments of the R ions to be equal to the free-ion values, the moment M_T of the T element is given by $M_T = M_s + M_R$. The composition dependence of M_T is shown in figures 3(a) and 3(b). It can be seen that M_T decreases monotonically with increasing Ni content. In order to discuss the influence of Ni substitution, a dashed line is shown which describes the case of simple dilution assuming that Ni is non-magnetic. It is clear that Ni contributes positively to the T-sublattice moment.

The temperature dependence of the magnetization of bulk samples at low fields is shown in figures 4(a) and 4(b). It can be seen that in all of the compounds, spin reorientations occur below room temperature. In the Er(Fe$_{1-x}$Ni$_x$)$_{11.3}$Nb$_{0.7}$ compounds, Ni substitution does not lead to a clear change of the spin-reorientation temperature T_{sr} for $x \leqslant 0.2$. For the compound with $x = 0.3$, two anomalies are found as shown by arrows. Two anomalies are

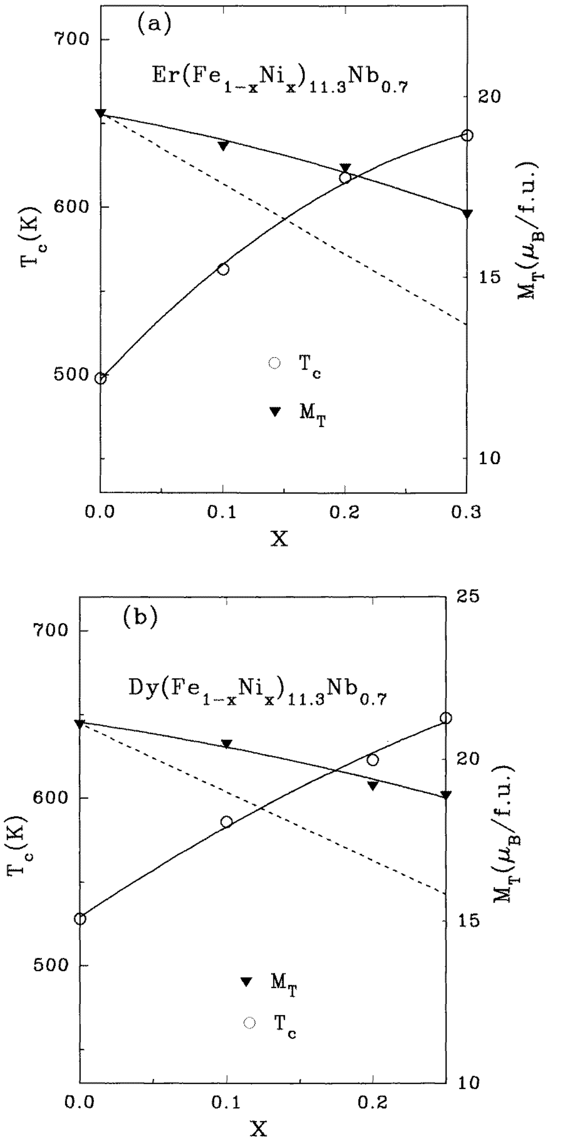

Figure 3. The composition dependence of the Curie temperature and the transition-metal moment at 5 K of R(Fe$_{1-x}$Ni$_x$)$_{11.3}$Nb$_{0.7}$ with R = (a) Er and (b) Dy. The broken lines represent the composition dependences of $M(T)$ if Ni is assumed to have zero magnetic moment.

also seen in the temperature dependence of the ac susceptibility of bulk samples as shown in figure 5(a). A similar behaviour has been observed in Er(Fe, Co)$_{11}$Ti compounds [11].

In R–T compounds, the easy-magnetization direction is determined by the interplay between the T-sublattice and R-sublattice anisotropies. The total anisotropy is the sum of the contributions. At room temperature and above, the T-sublattice anisotropy usually determines the magnetization direction, but at low temperatures the R-sublattice anisotropy may be dominant. We have shown [12] that in Y(Fe, Ni)$_{11.3}$Nb$_{0.7}$, the T-sublattice anisotropy

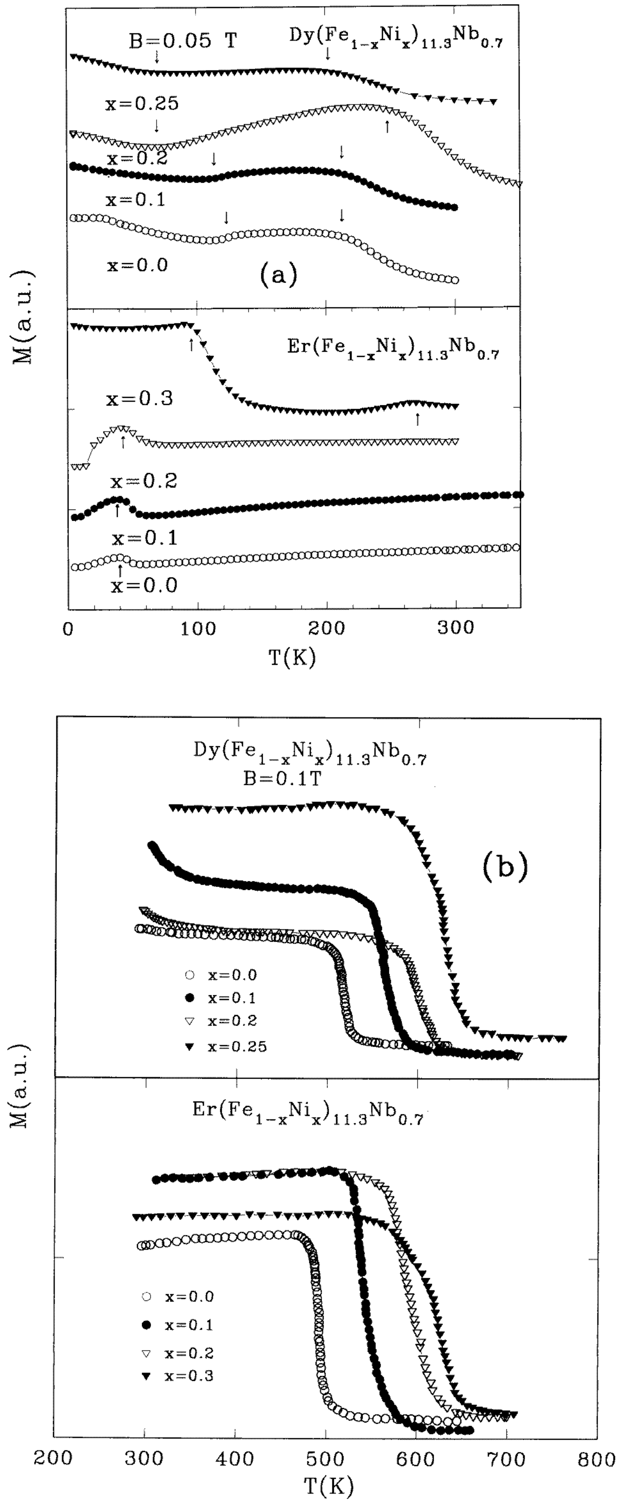

Figure 4. The temperature dependence from 5 to 350 K (a) of the magnetization at $B = 0.05$ T of R(Fe$_{1-x}$Ni$_x$)$_{11.3}$Nb$_{0.7}$ compounds with R = Er and Dy, and from room temperature up to 800 K (b) at $B = 0.1$ T with R = Er and Dy.

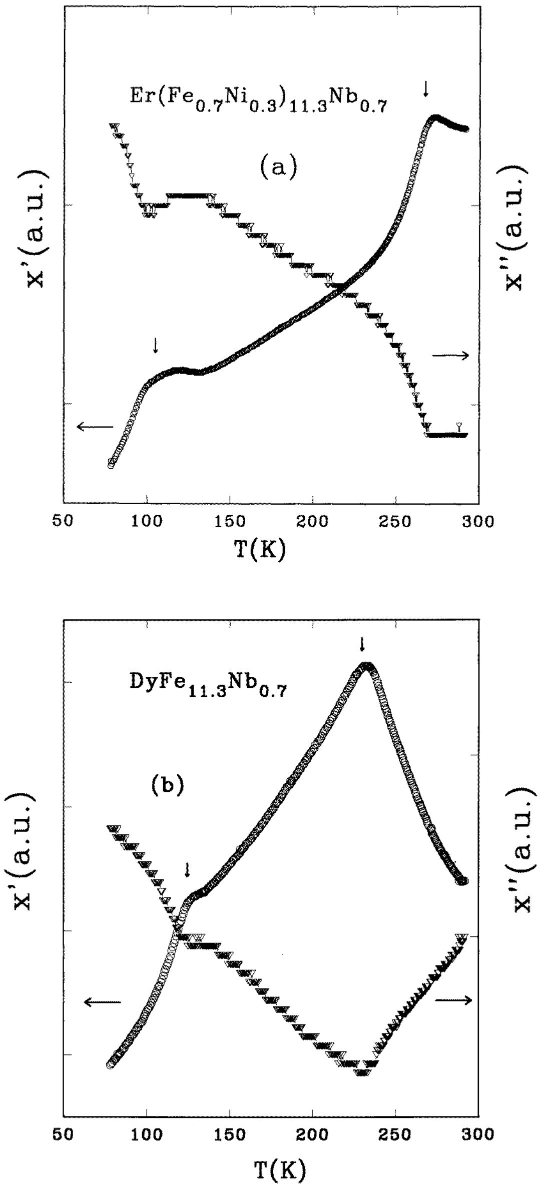

Figure 5. The temperature dependence of the ac susceptibility of (a) Er(Fe$_{0.7}$Ni$_{0.3}$)$_{11.3}$Nb$_{0.7}$ and (b) DyFe$_{11.3}$Nb$_{0.7}$.

is of easy-axis type. If we consider only the second-order crystal-field term, and within the strong-exchange-field approximation [9], the contribution of the rare earth to the second-order anisotropy constant, at room temperature, can be written as

$$K_1(R) = -\frac{3}{2}\alpha_J\langle r^2\rangle(3J^2 - J(J+1))A_2^0. \tag{1}$$

Here α_J is the second-order Stevens factor and A_2^0 the crystal-field parameter. Since for these compounds A_2^0 [4] is negative and α_J is positive for Er, the Er sublattice should give an easy-axis contribution. It has been reported [10] that in the compounds ErFe$_{10}$V$_2$ and ErFe$_{11}$Ti, the fourth- and sixth-order terms play an important role which leads to the occurrence of spin orientations. Therefore, it is likely that, just like in these compounds, the higher-order terms also play a critical role in Er(Fe, Ni)$_{11.3}$Nb$_{0.7}$ compounds. It has been well accepted that in R(Fe, M)$_{12}$ compounds the contributions of the three different Fe sites to the anisotropy are different. Hu *et al* [13] have reported that the anisotropy is probably mainly due to the orbital moment of Fe at 8i sites because the 8i hyperfine field shows a larger change upon spin reorientation. So, if Ni avoids the 8i sites for a small amount of Ni content, as is required in discussions on the influence of Ni substitution on T_C, Ni substitution would not have a big influence on the magnetic anisotropy. The observation (figure 4(a)) that the spin-reorientation temperature does not strongly depend on the Ni content indicates that this may be the case.

In all Dy(Fe$_{1-x}$Ni$_x$)$_{11.3}$Nb$_{0.7}$ compounds, two spin reorientations can be observed in the temperature dependence of the magnetization (figure 4(a)). In DyFe$_{11.3}$Nb$_{0.7}$ they are also observed in the temperature dependence of the ac susceptibility (figure 5(b)). This behaviour is similar to that of DyFe$_{11}$Ti for which these spin reorientations were studied in detail [13]. By comparison with this latter compound, we concluded that in our compounds, when temperature is increased, a spin reorientation from easy-plane to easy-cone first occurs at T_{sr1} and then the easy-cone structure becomes an easy-axis one at T_{sr2}.

4. Conclusion

The influence of Ni substitution for Fe on the magnetic and structural properties of RFe$_{11.3}$Nb$_{0.7}$ compounds with R = Er and Dy has been studied. Ni substitution does not lead to a change of the structure but results in a decrease of the lattice constants a and c. A clear increase of the Curie temperature and a decrease of the saturation magnetization are observed. For all of the compounds, the easy-magnetization direction at room temperature is along the c-axis. Spin reorientations are observed below room temperature.

Acknowledgments

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