Magnetovolume effect in ThMn_{12} -type Fe-rich $\text{R}(\text{Fe}, \text{Nb})_{12}$ -based compounds

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Abstract

We have measured the thermal expansion of several Fe-rich compounds with the ThMn_{12} structure. The series $\text{RFe}_{11.3}\text{Nb}_{0.7}$ ($\text{R} = \text{Y}, \text{Sm}, \text{Gd}, \text{Tb}, \text{Dy}, \text{Ho}$ and Er), $\text{Ho}(\text{Fe}_{1-x}\text{Ni}_x)_{11.3}\text{Nb}_{0.7}$ with $x = 0-0.3$, YFe_{11}Ti and $\text{YFe}_{10}\text{Mo}_2$ have been investigated in the temperature range 150–800 K. In the Fe-rich compounds with stabilizing element $\text{T} = \text{Nb}$ and Ti , a pronounced positive spontaneous volume magnetostriction has been observed below the Curie temperature. The effect of Ni substitution for Fe on the volume effect and on the Curie temperature has been analyzed studying the $\text{Ho}(\text{Fe}_{1-x}\text{Ni}_x)_{11.3}\text{Nb}_{0.7}$ compounds. The different magnitude of the magnetovolume effect observed in $\text{YFe}_{11.3}\text{Nb}_{0.7}$, YFe_{11}Ti and $\text{YFe}_{10}\text{Mo}_2$ is explained in terms of the classical model for itinerant ferromagnets. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

In the search for less expensive new permanent-magnet materials, considerable interest has been attracted by the Fe-rich rare-earth (R) intermetallic compounds [1]. Among these systems, ThMn_{12} -type rare-earth transition-metal compounds have attracted much more attention due to their

excellent magnetic properties and simple crystal structure (only one rare-earth site, 2a, and three transition-metal sites, 8i, 8j and 8f). The correlation between the magnetic properties and the lattice in the rare-earth-3d intermetallics has been the subject of many experimental and theoretical investigations [2]. It is well known that R_2Fe_{17} [3], $\text{R}_3(\text{Fe}, \text{T})_{29}$ [4] and $\text{R}_2\text{Fe}_{14}\text{B}(\text{C})$ [5–7] compounds undergo large spontaneous magnetostrictive deformations below their Curie temperature T_C . Compared with R_2Fe_{17} and $\text{R}_2\text{Fe}_{14}\text{B}$ systems [3,5–7], less investigations on the magnetovolume

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effects of ThMn_{12} -type compounds have been reported. The thermal-expansion behavior of the $\text{RFe}_{12-x}\text{T}_x$ system is more complicated and the stabilizing element T plays a crucial role [6]. As an example, in $\text{YFe}_{10}\text{V}_2$ and $\text{YFe}_{10.8}\text{Ti}_{1.2}$ an Invar-type thermal-expansion anomaly has been observed, while this anomaly almost disappears in the $\text{RFe}_{10}\text{Mo}_2$ compounds [6]. In this paper, a systematic study of the magnetic contribution to the thermal expansion of $\text{RFe}_{12-x}\text{Nb}_x$ and $\text{Ho}(\text{Fe}_{1-x}\text{Ni}_x)_{11.3}\text{Nb}_{0.7}$ compounds is presented. For comparison, the thermal expansion of $\text{YFe}_{11.3}\text{Ti}$ and $\text{YFe}_{10}\text{Mo}_2$ compounds is also reported.

2. Experimental

All compounds were prepared by arc melting appropriate amounts of the constituent elements in an argon gas atmosphere. The purity of the starting materials used is higher than 99.9%. The ingots were re-melted at least four times to promote mixing. The ingots of compounds with stabilizing element $\text{T}=\text{Ti}$ and Mo were annealed in Ar atmosphere at 1373 K for 24–48 h, followed by quenching in water. The single-phase quality of the compounds was checked by both X-ray-diffraction (XRD) analysis and thermomagnetic analysis (TMA). The magnetic properties of the compounds were measured in a vibrating-sample magnetometer (VSM) and a superconducting quantum interference device (SQUID). Thermal-expansion measurements were performed using a “push-rod” linear differential transformer method in the temperature range 150–1200 K.

3. Results and discussion

The temperature dependence of the linear thermal expansion (LTE), $\Delta l/l(T)$, and the LTE coefficient, $\alpha(T)$, for the $\text{RFe}_{11.3}\text{Nb}_{0.7}$ compounds is shown in Fig. 1. It can be seen that, for all compounds, $\Delta l/l(T)$ tends towards a linear behavior at temperatures above T_C and both $\Delta l/l(T)$ and $\alpha(T)$ exhibit a clear Invar-type anomaly around the Curie temperature. In order to estimate the spontaneous magnetostriction

Fig. 1. LTE and LTE coefficient for $\text{RFe}_{11.3}\text{Nb}_{0.7}$ compounds. The dashed line represents the lattice contribution. The arrows indicate the Curie temperatures.

giving rise to this anomaly, the lattice thermal expansion $(\Delta l/l)_{\text{lat}}$ has been subtracted from the measured thermal expansion. This lattice contribution can be extrapolated from the paramagnetic

to the ferromagnetic range, as shown in Fig. 1, by a dashed line. The extrapolation has been performed using the Grüneisen–Debye model with a Debye temperature $T_D = 450$ K [4]. We have calculated the spontaneous volume magnetostriction, ω_m , as $\omega_m = 3(\Delta l/l)_m$ with $(\Delta l/l)_m = (\Delta l/l)_{\text{exp}} - (\Delta l/l)_{\text{lat}}$, where $(\Delta l/l)_{\text{exp}}$ is the measured LTE. Comparing the results obtained on the $\text{RFe}_{11.3}\text{Nb}_{0.7}$ compounds with those on $\text{YFe}_{11.3}\text{Nb}_{0.7}$, it can be concluded that the major contribution to ω_m results from the spontaneous volume magnetostriction of the Fe sublattice. This is similar to the case of the $\text{R}_2\text{Fe}_{14}\text{B}$ and $\text{R}_2\text{Fe}_{14}\text{C}$ compounds [5–7]. It is well known that a spin-reorientation transition (SRT) takes place in $\text{TbFe}_{11.3}\text{Nb}_{0.7}$ and $\text{DyFe}_{11.3}\text{Nb}_{0.7}$ at temperatures $T_{\text{sr}} = 365$ and 224 K, respectively [8]. However, $\Delta l/l(T)$ and $\alpha(T)$ do not display any anomaly around T_{sr} , which makes a difference with respect to some other rare-earth intermetallics, as for example $\text{Er}_2\text{Fe}_{14}\text{B}$ and $\text{Nd}_3(\text{Fe,Ti})_{29}$ compounds [4,6]. ω_m extends to temperatures above T_C reflecting the existence of short-range magnetic order in the paramagnetic state. In order to check the influence of small changes of the Nb concentration on the thermal expansion, we have measured $\Delta l/l(T)$ of $\text{TbFe}_{12-x}\text{Nb}_x$ and $\text{DyFe}_{12-x}\text{Nb}_x$ for $x = 0.6–0.8$ (the formation range of a single phase with ThMn_{12} -type structure). Our experimental results indicate that a change of the Nb content within this range does not have any clear influence on $\Delta l/l(T)$ and T_C , even though the saturation magnetization M_s and T_{sr} decrease clearly with increasing x [8].

Fig. 2 displays the temperature dependence of $\Delta l/l(T)$ for the $\text{Ho}(\text{Fe}_{1-x}\text{Ni}_x)_{11.3}\text{Nb}_{0.7}$ compounds with $x = 0, 0.1, 0.2, 0.25$ and 0.3 . In all the compounds there exists a positive spontaneous volume magnetostriction below T_C . ω_m monotonically decreases with increasing Ni content. Comparison with the previous results [9] shows that the influence of Ni substitution on ω_m differs from that due to Co substitution. Substitution of Fe by Co in YFe_{11}Ti leads to a maximum of ω_m at about 30% Co concentration, followed by a rapid decrease when increasing Co content, and finally ω_m disappears close to the pure Co-based compound [10]. It has been reported that the magneto-

Fig. 2. LTE and LTE coefficient for $\text{Ho}(\text{Fe}_{1-x}\text{Ni}_x)_{11.3}\text{Nb}_{0.7}$ compounds. The dashed line represents the lattice contribution. The arrows indicate the Curie temperatures.

volume effect observed in the thermal expansion of the R_2Fe_{17} compounds is a characteristic feature of the Fe matrix, being hardly dependent on the R-partner and not observed in R_2Co_{17} and R_2Ni_{17} compounds [3]. It can be expected that for the $\text{R}(\text{Fe}_{1-x}\text{Ni}_x)_{12-y}\text{Nb}_y$ compounds the Invar-type anomaly will also disappear with further increasing Ni content. Unfortunately, in the present case the maximum Ni concentration in $\text{Ho}(\text{Fe}_{1-x}\text{Ni}_x)_{11.3}\text{Nb}_{0.7}$ compounds is limited to $x = 0.3$, and therefore the disappearance of the

spontaneous magnetostriction with increasing Ni content would be outside of our studied concentration range. It is well known that the Invar effect in R-Fe based compounds is related to the weak ferromagnetic character of 3d magnetic moments. As in the case of Y(Fe,Ni)₁₁Ti compounds [1], the change of the 3d magnetism with increasing Ni content (from weak to strong ferromagnetic) may be the origin of the observed evolution of the magnetovolume effect in the Ho(Fe,Ni)_{11.3}Nb_{0.7} series.

In order to study the origin of the Invar-type anomaly in ThMn₁₂-type compounds, we have measured the thermal expansion of YFe₁₁Ti and YFe₁₀Mo₂. The temperature dependence of $\Delta l/l(T)$ for YFe₁₁Ti, YFe₁₀Mo₂ and YFe_{11.3}Nb_{0.7} is shown in Fig. 3, together with that of YFe_{11.3}Nb_{0.7} for comparison. It can be seen that, for both YFe₁₁Ti and YFe_{11.3}Nb_{0.7}, a pronounced positive spontaneous magnetostriction occurs, while for YFe₁₀Mo₂ the Invar-type anomaly seems to be much less pronounced. It has been observed

that the existence of the Invar effect is related to a strong dependence of T_C and the magnetization with the interatomic distances in the lattice [11]. Therefore, it is interesting to compare our results with the reported pressure experiments on YFe₁₁Ti, where a variation of the Fe magnetic moment with pressure was found, given by $d\mu_{Fe}/dp = -3.4 \times 10^{-3}$ kbar [12]. This is a confirmation of the tight relation between magnetic and lattice effects in these compounds. The reported results can be understood within the classical model of itinerant ferromagnetism in which the magnetovolume effect is related to the gradient of the density of states (DOS) at the Fermi level, E_F . If E_F lies in an energy region with a steep slope of the DOS curve, small changes in the position of E_F could induce large changes in the magnetic moment [13]. The theoretical calculations for YFe₁₀Mo₂ and YFe₁₁Ti show that the slope of the DOS curve at E_F in YFe₁₁Ti is much steeper than that in YFe₁₀Mo₂ [14], in good agreement with our results.

4. Conclusions

A positive spontaneous magnetostriction ω_m has been observed below the Curie temperature T_C for RFe_{11.3}Nb_{0.7} (R = Y, Sm, Gd, Tb, Dy, Ho, Er), Ho(Fe_{1-x}Ni_x)_{11.3}Nb_{0.7} with $x = 0-0.3$ and YFe₁₁Ti. Ni substitution leads to a decrease in ω_m and an increase in T_C . No pronounced anomaly is observed in either $\Delta l/l(T)$ or $\alpha(T)$ at the spin-reorientation temperature T_{sr} for the TbFe_{12-x}Nb_x and DyFe_{12-x}Nb_x compounds. ω_m extends to temperatures above T_C , reflecting the existence of short-range magnetic order in the paramagnetic state. For YFe₁₀Mo₂, the magnetic contribution to the thermal expansion is small compared with the pronounced positive ω_m , which takes place in YFe₁₁Ti and YFe_{11.3}Nb_{0.7}. The results follow the trend of the classical model for itinerant ferromagnetism.

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Fig. 3. LTE and LTE coefficient for YFe_{11.3}Nb_{0.7}, YFe₁₁Ti and YFe₁₀Mo₂. The dashed line represents the lattice contribution. The arrows indicate the Curie temperatures.

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