UvA-DARE (Digital Academic Repository)

Magnetic properties of R(Fe,Mn) 11 Ti compounds

Zhao, T.; Kou, X.C.; Zhang, Z.D.; Sun, X.K.; Chuang, Y.C.; de Boer, F.R.

DOI

[10.1063/1.361987](https://doi.org/10.1063/1.361987)

Publication date

1996

Published in

Journal of Applied Physics

[Link to publication](#)

Citation for published version (APA):

Zhao, T., Kou, X. C., Zhang, Z. D., Sun, X. K., Chuang, Y. C., & de Boer, F. R. (1996). Magnetic properties of R(Fe,Mn) 11 Ti compounds. *Journal of Applied Physics*, 79, 6324-6326. <https://doi.org/10.1063/1.361987>

General rights

It is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), other than for strictly personal, individual use, unless the work is under an open content license (like Creative Commons).

Disclaimer/Complaints regulations

If you believe that digital publication of certain material infringes any of your rights or (privacy) interests, please let the Library know, stating your reasons. In case of a legitimate complaint, the Library will make the material inaccessible and/or remove it from the website. Please Ask the Library: <https://uba.uva.nl/en/contact>, or a letter to: Library of the University of Amsterdam, Secretariat, Singel 425, 1012 WP Amsterdam, The Netherlands. You will be contacted as soon as possible.

Magnetic properties of $R(\text{Fe,Mn})_{11}\text{Ti}$ compounds

T. Zhao

Institute of Metal Research, Academia Sinica, Shenyang 110015, People's Republic of China; Van der Waals-Zeeman Laboratory, University of Amsterdam, 1018 XE, Amsterdam, The Netherlands

X. C. Kou

Institut für Experimentalphysik, Technische Universität Wien, Wiedner Hauptstrasse 8-10, A-1040 Wien, Austria

Z. D. Zhang, X. K. Sun, and Y. C. Chuang

Institute of Metal Research, Academia Sinica, Shenyang 110015, People's Republic of China

F. R. de Boer

Van der Waals-Zeeman Laboratory, University of Amsterdam, 1018 XE Amsterdam, The Netherlands

High-field magnetization measurements have been performed on both free-powder samples and magnetically aligned samples of $R(\text{Fe,Mn})_{11}\text{Ti}$ ($R=\text{Y, Nd, Sm, Gd, Er}$) compounds at 4.2 K in a step field up to 28 T. The temperature dependence of ac susceptibilities of $R(\text{Fe,Mn})_{11}\text{Ti}$ has been measured in a temperature range from 4.2 to 800 K. It has been found that both the magnetic moment of the transition-metal sublattice and the Curie temperature of $R\text{Fe}_{11-x}\text{Mn}_x\text{Ti}$ compounds decrease with increasing x . Spin reorientations occur in $\text{ErFe}_{11-x}\text{Mn}_x\text{Ti}$ compounds as the result of competition between the uniaxial anisotropy of the transition-metal sublattice and the planar or conical anisotropy of the Er sublattice. The intersublattice exchange constants n_{RT} of $\text{ErFe}_{11-x}\text{Mn}_x\text{Ti}$ compounds have been deduced by the high-field free-powder method. The effect of the substitution of Fe by Mn on the magnetic anisotropies of $R(\text{Fe,Mn})_{11}\text{Ti}$ with $R=\text{Y, Nd, Sm}$ has been investigated. First-order magnetization processes take place in $\text{SmFe}_{11-x}\text{Mn}_x\text{Ti}$ compounds when the external field is applied perpendicular to the alignment direction. © 1996 American Institute of Physics. [S0021-8979(96)34808-3]

I. INTRODUCTION

In the early 1980s, many efforts have been made to produce iron-rich compounds with the ThMn_{12} structure by substituting Mn by Fe in RMn_{12} compounds.¹ However, since the solid solubility of Fe in $\text{YMn}_{12-x}\text{Fe}_x$ limits to $x=8$, this substitution cannot lead to an Fe-rich compound. Recently, the Fe-rich $R(\text{Fe,Mn})_{12}$ compounds with the ThMn_{12} structure have been obtained by adding a small amount of a third element, such as Ti, V, Cr, Mo, W, and Al.² So it is possible to study the effect of Mn substitution on the magnetic properties of Fe-rich rare-earth transition-metal compounds with the ThMn_{12} -type structure, in which the Mn is added as a fourth element to substitute part of the iron. In the present work, we have chosen $R\text{Fe}_{11}\text{Ti}$ as the starting compound, and prepared the $R\text{Fe}_{11-x}\text{Mn}_x\text{Ti}$ compounds with $x=0, 1, 2, 3, 4$. The magnetic properties of these compounds have been investigated by high-field magnetization measurements up to 21 T at 4.2 K and ac-susceptibility measurements from 4.2 to 800 K.

II. SAMPLE PREPARATION

Polycrystalline $R\text{Fe}_{11-x}\text{Mn}_x\text{Ti}$ ingots with $R=\text{Y, Nd, Sm, Gd, and Er}$ and $x=0, 1, 2, 3, 4$ have been prepared by induction-melting appropriate amounts of pure materials of a purity of at least of 99.99 wt %. The ingots were remelted two times to achieve homogeneity. Weight losses during the melting due to evaporation of the rare-earth element and Mn were compensated for by starting with an excess of 3 wt % R (with respect to the R content) and 5 wt % Mn (with respect to the Mn content). The as-cast ingots were wrapped in Ta foil and sealed in a pre-evacuated and then argon-gas-filled

quartz tube, followed by annealing at 1273 K for three weeks and then water-quenched to avoid possible metallographic phase transitions during the cooling process.

The crystal structures of the samples were checked by x-ray diffraction. It was found most of the samples have the ThMn_{12} -type tetragonal structure and a small amount of $\alpha\text{-Fe}$ exists as a second phase.

III. RESULTS AND DISCUSSION

The high-field measurements at 4.2 K were performed on free-powder samples of $R\text{Fe}_{11-x}\text{Mn}_x\text{Ti}$ compounds to study saturation magnetization and exchange interaction. For the high-field free-powder (HFFP) measurements,^{3,4} fine-powder ($<40\text{ }\mu\text{m}$) samples were loosely loaded into the sample holders. These particles can be considered as monocrystalline and are free to rotate in the external field so that the total magnetic moment of the samples is always parallel to the external field direction. The values for the saturation magnetization obtained in this way are tabulated in Table I. One can see that, for $R\text{Fe}_{11-x}\text{Mn}_x\text{Ti}$ ($R=\text{Y, Nd, Sm}$) compounds, the saturation magnetization in these compounds decreases upon Mn substitution. In the $\text{YFe}_{11-x}\text{Mn}_x\text{Ti}$ compounds, since Y is nonmagnetic, the magnetic moment of the transition-metal sublattice is equal to the saturation magnetization. In $\text{NdFe}_{11-x}\text{Mn}_x\text{Ti}$ and $\text{SmFe}_{11-x}\text{Mn}_x\text{Ti}$, if we assume that the $4f$ electrons of rare-earth element are well localized, the moment of the transition-metal sublattice (M_T) can be obtained by subtracting the free-ion moment of the rare-earth element (M_R) from the saturation magnetization (M_s). The obtained M_T values are listed in Table II. In $\text{GdFe}_{11-x}\text{Mn}_x\text{Ti}$ and $\text{ErFe}_{11-x}\text{Mn}_x\text{Ti}$ compounds, M_s first

TABLE I. Saturation magnetization of $\text{RFe}_{11-x}\text{Mn}_x\text{Ti}$ compounds.

M_s ($\mu_B/\text{f.u.}$)	Y	Nd	Sm	Gd	Er
$x=0$	20.0	21.7	19.6	12.2	10.8
$x=1$	15.4	17.2	16.4	9.3	6.6
$x=2$	12.5	15.1	10.2	4.0	2.4
$x=3$	7.4	13.7	7.5	2.6	1.8
$x=4$	4.2	6.9	4.7	2.7	4.6

decreases upon the Mn substitution from $x=0$ to $x=3$, and then increases. This behavior is due to the antiparallel configuration of the moments of the transition-metal sublattice and the heavy-rare-earth sublattice. In $\text{ErFe}_{11}\text{Ti}$ and $\text{GdFe}_{11}\text{Ti}$, the magnetic moment of the Fe sublattice is much larger than that of the rare-earth sublattice so that the total magnetic moment equals to $M_T - M_R$. When Fe is substituted by Mn, the moment of the transition-metal sublattice decreases and causes a decrease of the saturation magnetization. If the moment of the transition-metal sublattice becomes smaller than that of the rare earth upon the Mn substitution, the total magnetic moment, which is now $M_R - M_T$, will increase (the case of $x=4$) with decreasing M_T . The values of the moments of the transition-metal sublattice are obtained by $M_T = M_R \pm M_s$ accordingly (see Table II).

For all investigated $\text{RFe}_{11-x}\text{Mn}_x\text{Ti}$ compounds, M_T decreases monotonically with increasing x . If the mean Fe moment were not affected by substitution and the Mn ion were nonmagnetic, M_T would decrease linearly by $M_T(x) = M_T(0)(11-x)/11$, where $M_T(x)$ and $M_T(0)$ are the saturation magnetizations of $\text{RFe}_{11-x}\text{Mn}_x$ and RFe_{11}Ti , respectively. The experimental results obviously deviate from this line, which is similar to the case of $\text{R}(\text{Co}, \text{Mn})_{11}\text{Ti}$ compounds.⁵ One possible interpretation for the relatively fast decrease of M_T could be that the magnetic moment of iron is affected by the surrounding of Mn atoms which might be coupled antiferromagnetically with the Fe moment.¹ Another possible reason for this is that the Mn atom which is larger than Fe prefers to substitute the Fe atom on the 8i site where Fe has the largest moment in RFe_{11}Ti .¹

FIG. 1. Magnetic isotherms at 4.2 K of $\text{ErFe}_{11-x}\text{Mn}_x\text{Ti}$ compounds measured on powder particles that are free to rotate in the sample holder.TABLE II. Magnetic moments of the transition-metal sublattice in $\text{RFe}_{11-x}\text{Mn}_x\text{Ti}$ compounds.

M_T ($\mu_B/\text{f.u.}$)	Y	Nd	Sm	Gd	Er
$x=0$	20.0	18.4	18.9	19.2	19.8
$x=1$	15.4	13.9	15.7	16.3	15.6
$x=2$	12.5	11.8	9.4	11.0	11.4
$x=3$	7.4	10.4	6.8	9.6	7.2
$x=4$	4.2	3.6	4.0	4.3	4.4

HFFP measurements are usually used to get information about the intersublattice interaction in heavy-rare-earth transition-metal compounds.^{3,4} If the external field is so high that the collinear configuration of the magnetic moments of the rare-earth and transition-metal sublattices is broken, the coupling constant n_{RT} can be obtained from the slope of the bending process if the anisotropy of at least one of the sublattices is negligible. In external fields up to 28 T, the bending process can be observed in $\text{ErFe}_{11-x}\text{Mn}_x\text{Ti}$ compounds with $x=1, 2$, and 3 (see Fig. 1). Hurley⁶ has measured the free-powder magnetization process of $\text{ErFe}_{11}\text{Ti}$ and its first critical field is 35 T. In the present work, the first critical fields have been determined to be 23, 10.5, and 0 T for $x=1, 2$, and 3, respectively. The coupling constants deduced from the slope in the bending section are 4.5, 4.0, and 4.5 T f.u./ μ_B for $x=1, 2$, and 3, respectively. It seems that Mn substitution has no significant influence on n_{RT} . However, no bending process is found in $\text{GdFe}_{11-x}\text{Mn}_x\text{Ti}$ compounds. This may be due to the relatively large n_{RT} in Gd compounds.

To investigate the effects of Mn substitution on the anisotropy of $\text{R}(\text{Fe}, \text{Mn})_{11}\text{Ti}$ ($\text{R}=\text{Sm}, \text{Nd}, \text{Y}$) compounds. The high-field magnetization was measured on aligned samples with the magnetic field parallel and perpendicular to the alignment direction. In $\text{YFe}_{11-x}\text{Mn}_x\text{Ti}$ compounds, the anisotropy field B_a decreases upon Mn substitution. The values obtained for B_a are 4, 3.5, and 2.5 T for $x=0, 1, 2$, respectively. The Curie temperature for compounds with $x>2$ is

FIG. 2. Magnetic isotherms at 4.2 K of $\text{SmFe}_{11-x}\text{Mn}_x\text{Ti}$ compounds measured on magnetically aligned powders. Open marks correspond to the field parallel to the alignment direction and filled marks to the field perpendicular to the alignment direction. The dots correspond to the measurements in a continuously varying field. The solid lines are guides to the eye.

TABLE III. Curie temperatures of $\text{RFe}_{11-x}\text{Mn}_x\text{Ti}$ compounds.

T_c (K)	Y	Nd	Sm	Er	Gd
$x=0$	530	550	595	515	605
$x=1$	455	465	510	425	530
$x=2$	370	405	460	305	430
$x=3$	200	285	115	210	330
$x=4$	105	215	85	90	...

lower than room temperature, so we cannot prepare well-aligned samples of these compounds at room temperature. For $\text{NdFe}_{11}\text{Ti}$, the magnetization along the alignment direction is smaller than that perpendicular to the alignment direction. A possible interpretation for this may be that the weak easy-axis anisotropy of $\text{NdFe}_{11}\text{Ti}$ at room temperature⁷ changes to an easy-cone anisotropy with a cone angle larger than 45° at 4.2 K. With increasing x , the magnetization parallel to the orientation direction becomes relatively large indicating that Mn substitution decreases the cone angle at low temperature or causes an easy-cone anisotropy at room temperature. Of more interest are the $\text{SmFe}_{11-x}\text{Mn}_x\text{Ti}$ compounds in which first-order magnetization process (FOMP)-like anomalies appear in the magnetization curves measured along the direction perpendicular to the orientation direction (Fig. 2). These anomalies are similar to the one found by Hu *et al.*⁷ in $\text{SmFe}_{11}\text{Ti}$. The critical field, corresponding to the maximum of the first derivative of the magnetization curve, decreases upon Mn substitution. The critical fields in $\text{SmFe}_{11}\text{Ti}$ and $\text{SmFe}_{10}\text{MnTi}$ are 10.2 and 8.9 T, respectively. In $\text{SmFe}_9\text{Mn}_2\text{Ti}$, the anomaly becomes hard to distinguish because of the poor alignment of the powder at room temperature, and the critical field decreases to about 8 T. These anomalies may be due to field-induced first-order transitions or quasi-FOMPs.⁸

The ac susceptibilities of $\text{RFe}_{11-x}\text{Mn}_x\text{Ti}$ compounds were measured in the temperature range from 4.2 to 800 K. The obtained T_c values are listed in Table III. T_c decreases monotonically with increasing x . This is similar to the concentration dependence of M_T . Spin reorientations from easy axis at high temperature to easy cone or easy plane at low temperature were found in $\text{ErFe}_{11-x}\text{Mn}_x\text{Ti}$ compounds. At T_{SR} and above, the uniaxial iron anisotropy usually determines the magnetization direction but at lower temperatures the rare-earth anisotropy may be dominant. The T_{SR} corre-

sponds to the minimum of $d\chi'/dT$. The T_{SR} for compounds with $x=0, 1, 2, 3$ are 48, 50.5, 99.4, and 171.4 K, respectively. The decrease of T_{SR} with increasing x may imply that the uniaxial anisotropy of the transition-metal sublattice decreases upon Mn substitution.

In conclusion, both the magnetic moments of the transition-metal sublattice and the Curie temperatures of the $\text{RFe}_{11-x}\text{Mn}_x\text{Ti}$ ($x=0, 1, 2, 3, 4$) compounds decrease with increasing x . The introduction of Mn atoms, which are non-magnetic or possess a magnetic moment antiparallel to the Fe moments, gives rise to a decrease of the mean Fe moment. In $\text{RFe}_{11-x}\text{Mn}_x\text{Ti}$, the transition-metal sublattice possesses uniaxial anisotropy which decreases upon Mn substitution. In $\text{RFe}_{11-x}\text{Mn}_x\text{Ti}$ ($\text{R}=\text{Nd}, \text{Er}$), there exists competition between the uniaxial anisotropy of the transition-metal sublattice and the planar or conical anisotropy of the rare-earth sublattice, which gives rise to spin reorientations in the $\text{ErFe}_{11-x}\text{Mn}_x\text{Ti}$ compounds. FOMP-like anomalies found in $\text{SmFe}_{11-x}\text{Mn}_x\text{Ti}$ compounds indicate that the high-order anisotropies play an important role in the magnetization processes of these compounds.

ACKNOWLEDGMENTS

This work has been supported by the exchange programme between China and the Netherlands, the National Natural Sciences Foundation of China, the Sciences and Technology Commission of Shenyang, the President Foundation of the Chinese Academy of Science, and the K. C. Wong Education Foundation of Hong Kong.

- ¹Y. C. Yang, B. Kebe, W. James, J. Deportes, and W. Yelon, *J. Appl. Phys.* **52**, 2077 (1981).
- ²H. S. Li and J. D. M. Coey, in *1991 Ferromagnetic Materials*, edited by K. H. J. Buschow and E. P. Wohlfarth (North Holland, Amsterdam, 1991), Vol. 6.
- ³R. Verhoef, F. R. de Boer, J. J. M. Franse, C. J. M. Dennisen, T. H. Jacobs, and K. H. J. Buschow, *J. Magn. Magn. Mater.* **80**, 41 (1989).
- ⁴R. Verhoef, R. J. Radwanski, and J. J. M. Franse, *J. Magn. Magn. Mater.* **81**, 176 (1990).
- ⁵J. Allemand, C. Bertrand, J. Le Roy, J. M. Moreau, D. Paccard, M. A. Fremy, and D. Givord, in *Concerted European Action on Magnets (CEAM)*, edited by I. V. Harris and R. Hanitsch (Elsevier, London, 1989), p. 98.
- ⁶D. P. F. Hurley, Ph.D. thesis, The University of Dublin, 1993.
- ⁷B. P. Hu, H. S. Li, J. P. Gavigan, and J. M. D. Coey, *J. Phys.* **1**, 755 (1989).
- ⁸T. Zhao, X. K. Sun, Z. D. Zhang, Q. Wang, Y. C. Chuang, and F. R. de Boer, *J. Magn. Magn. Mater.* **104**, 2119 (1992).