

NITROGENATION OF THE  $RFe_{10}Mo_2$  ( $R$  = RARE EARTH) COMPOUNDS  
WITH  $ThMn_{12}$  TYPE STRUCTURE

M. Anagnostou, C. Christides and D. Niarchos

Institute of Materials Science, N.C.S.R. "DEMOKRITOS"  
153 10 Ag. Paraskevi Attikis, Greece

Received 30 January 1991 by P. Burlet

Interstitial nitrides with the general formula  $RFe_{10}Mo_2N_x$  have been prepared for  $R = Y, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm$  and  $Lu$ . All compounds have the  $ThMn_{12}$  tetragonal structure with unit cell volumes about 3% larger than the non nitrogenated parent compounds. Curie temperature are enhanced in the nitrides from 30% in  $Gd$  up to 80% in  $Lu$  compounds. The  $NdFe_{10}Mo_2N_x$  alloy exhibits an uniaxial anisotropy with  $B_A > 9$  Tesla at 4.5 K.

Introduction

Recently, the absorption of nitrogen with a gas-solid reaction from the  $R_2Fe_{17}$  intermetallic compounds has produced a new family of interstitial nitrides with general formula  $R_2Fe_{17}N_x$  ( $2.3 < x < 2.9$ )<sup>1</sup>. The considerably improved magnetic properties of this new series over the 2:17 phase, lead to an effort of introducing nitrogen in the structures of other known rare earth-iron rich series of alloys.

We report here the preparation of a new series of nitrides with general formula  $RFe_{10}Mo_2N_x$  and tetragonal structure of the  $ThMn_{12}$  type. The lattice constants, the Curie temperatures and the saturation magnetization of the  $RFe_{10}Mo_2$  and  $RFe_{10}Mo_2N_x$  compounds are presented in order to show the lattice expansion, the increase of the  $T_c$  and the enhancement of the anisotropy field values by the  $N_2$  absorption.

Experimentals

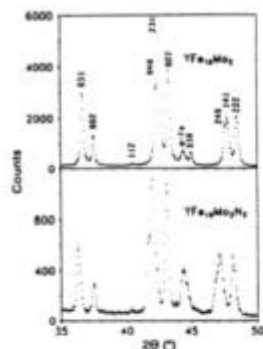
The  $RFe_{10}Mo_2$  ( $R = Y, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm$  and  $Lu$ ) compounds were first prepared by arc-melting of the constituents (all 99.99% pure) followed by an annealing in vacuum at 850°C for a week. X-ray diffraction showed these samples to be single phase with the 1:12 tetragonal structure. The annealed samples were grounded in a very fine powder (<10 $\mu$ m) and heated in an atmosphere of purified  $N_2$  gas for 2 1/2 hours at 500°C. X-ray patterns of the samples were taken in a Siemens D-500 diffractometer with Cu-K $\alpha$  radiation.

From the X-ray diagrams of the nitrated samples we conclude that the nitrogenation process reaches completion since the diffraction peaks of the nitrides were shifted considerably to lower diffraction angles relative to those of the original  $RFe_{10}Mo_2$  compounds and remain unchanged for longer nitrogenation times.

The Curie temperatures were determined with a thermogravimetric balance (Perkin Elmer 7/4) and saturation magnetizations were deduced at 4.5K from the high field part of  $M$  vs  $H$  curves, measured in a vibrating sample magnetometer. The maximum field used was 2T and the  $M_s$  values were calculated using the law of approach to saturation<sup>2</sup>.

Results and Discussion

The X-ray diffraction patterns for  $YFe_{10}Mo_2$  and  $YFe_{10}Mo_2N_x$  are given in fig. 1, which show that in the nitrides the structure remains the same. In Table 1 the lattice parameters for the 1:12 nitrides and for the non nitrogenated parent compounds as well as the percentage of the resulting volume expansion in nitrides are listed. In Table 2 the obtained Curie temperatures  $T_c$  and saturation magnetization  $M_s$  for both series of alloys are tabulated. Figure 2 shows the considerable increase of the  $T_c$  values in the nitrides. It is obvious that an enhancement of the exchange interactions is induced from the lattice expansion in nitrides. An interesting feature in fig. 2 is that the commonly observed strongly peaked shape of the  $R$  dependence of the Curie temperature is found only in  $RFe_{10}Mo_2$ .



1. X-ray patterns, in the range of the most intensive peaks, for the  $YFe_{10}Mo_2$  and  $YFe_{10}Mo_2N_x$ .

competition between the planar anisotropy of Nd and the uniaxial anisotropy of the Fe sublattice a spin reorientation transition (SRT) occurs at low temperatures <sup>4,5</sup> and the total anisotropy field is negligible in all temperature range where these compounds are magnetic.

Magnetic measurements on oriented  $NdFe_{10}Mo_2N_x$  samples parallel and perpendicular to the orientation axis reveal an appreciable anisotropy field  $B_A$  around 7T at RT which increases at lower temperatures up to a value around 10T at 4.5K. In fig. 3 are shown the plots of  $M_{||}$  and  $M_{\perp}$  vs H for an oriented sample measured at 4.5K and RT. The reported values of the anisotropy fields are deduced by linear extrapolation of the high field part of

Table 1: The lattice parameters of the  $RFe_{10}Mo_2N_x$  and  $RFe_{10}Mo_2$  series and the percentage of the lattice expansion in the nitrides

R	$RFe_{10}Mo_2N_x$		$RFe_{10}Mo_2$		$\Delta V/V$ (%)
	a (Å)	c (Å)	a (Å)	c (Å)	
Y	8.670	4.799	8.553	4.798	2.8
Nd	8.671	4.870	8.589	4.788	3.6
Sm	8.671	4.850	8.580	4.798	3.2
Gd	8.660	4.819	8.568	4.802	2.5
Tb	8.664	4.820	8.546	4.785	3.5
Dy	8.674	4.812	8.538	4.790	3.7
Ho	8.659	4.799	8.523	4.788	3.4
Er	8.656	4.796	8.517	4.785	3.5
Tm	8.650	4.780	8.513	4.781	3.2
Lu	8.656	4.773	8.511	4.780	3.3

and is smoothed out in  $RFe_{10}Mo_2N_x$  series. The conclusion one may derive from this T<sub>c</sub> behavior is that the R-Fe interaction is weakened and the Fe-Fe interaction is almost doubled in the nitrides. This is in complete agreement with that observed in the  $R_2Fe_{17}$  nitrides <sup>3</sup>.

The most interesting result is the induced anisotropy for the  $NdFe_{10}Mo_2N_x$  compound. It is well known that in  $RFe_{10}T_2$  (T= V, Mo, Ti) <sup>4,5</sup> compounds the Nd anisotropy tends for an alignment of the magnetic moment in the (a,b) plane. As a result of the

the  $M_{||}$  and  $M_{\perp}$  curves. Thermomagnetic measurements in the range 5-650K do not show any SRT indicating that the anisotropy is always uniaxial.

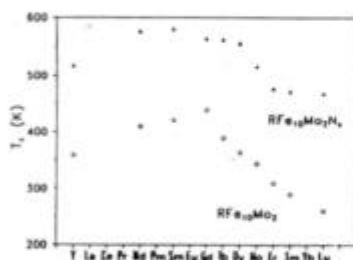
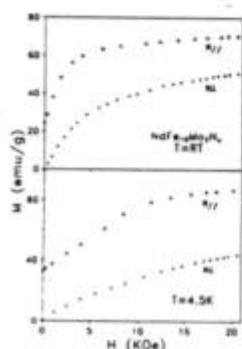
The tremendous increase of the anisotropy field in Nd nitride together with the observed weakening of R-Fe interactions could be indicative for a site occupation of the  $N_2$  atoms around the R site in the  $ThMn_{12}$  structure.

#### Conclusions

A new series of  $RFe_{10}Mo_2N_x$  nitrides has been synthesized from the  $RFe_{10}Mo_2$

Table 2: Curie temperatures and saturation magnetizations (at 4.5K) for the  $RFe_{10}Mo_2N_x$  and  $RFe_{10}Mo_2$  series.

R	$RFe_{10}Mo_2N_x$		$RFe_{10}Mo_2$		$\Delta T_c/T_c(\%)$
	$T_c(K)$	$M_s(emu/g)$	$T_c(K)$	$M_s(emu/g)$	
Y	518	108	360	87	44
Nd	577	91	410	102	41
Sm	581	97	421	94	38
Gd	565	69	440	51	28
Tb	563	39	390	30	44
Dy	557	26	365	27	53
Ho	517	37	345	21	50
Er	478	53	310	22	54
Tm	473	70	290	33	63
Lu	469	100	260	64	80

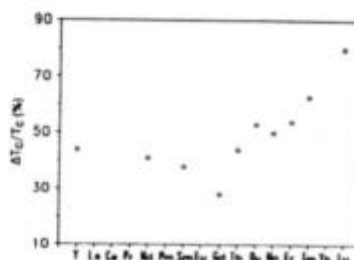
2. Curie temperatures for  $RFe_{10}Mo_2$  and  $RFe_{10}Mo_2N_x$  (R= rare earth).3. Plot of  $M_{//}$  and  $M_{\perp}$  versus  $H$  for an oriented sample of  $NdFe_{10}Mo_2N_x$  at 4.5K and RT.

compounds with the  $ThMn_{12}$  type structure. The structure of the nitrides is related to the parent 1:12 compounds and the unit cell volume increases by 2.8-3.7% which is nearly half of the lattice expansion observed in  $R_2Fe_{17}N_x$  compounds<sup>2</sup>.

A plot of the percentage increase of  $T_c$  vs R in fig. 4 shows that there is no uniform enhancement of  $T_c$  values across the R series and that a minimum enhancement appears for the Gd compound.

Appreciable anisotropy is found for the Nd compound but the saturation moment is not very high (table 2) compared to other permanent magnet compounds.

The larger  $M_s$  values observed in the nitrides with non magnetic rare earth (R= Y, Lu) at 4.5K are very peculiar and further magnetic

4. The percentage increase of  $T_c$  in the  $RFe_{10}Mo_2$  nitrides.

measurements which will be published elsewhere could explain this phenomenon.

Acknowledgements - This work was partially supported by the BRITE/EURAM program of the E.C.

#### References

1. J.M.D. Coey and Hong Sun, J. Magn. Magn. Mat. 87 (1990) L251.
2. H. Sun, J.M.D. Coey, Y. Otani and D.P.F. Hurley, J. Phys. Cond. Mat. 2 (1990), 6465.
3. S. Chikazumi, Physics of Magnetism, John Willey and sons 1964.
4. Bo Ping Hu, Hong Shuo Li, J. P. Gavigan and J.M.D. Coey, J. Phys. Cond. Mat. 1 (1989), 755.
5. C. Christides, A. Kostikas, A. Simopoulos, D. Niarchos and G. Zouganelis, J. Magn Magn. Mat. 86 (1990), 367.