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Magnetic behaviour of Fe/Nd multilayers

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Abstract The magnetic behaviour of Fe/Nd multilayered thin films as deposited and after thermal annealing is reported. The multilayered samples were analyzed with CEMS and with a VSM. The results indicate strong interdiffusion and phase formation of the constituents. The phases formed could not be identified on basis of the bulk FeNd system phase diagram. Boron implanted samples were also analyzed in this study. This article reports the preliminary results of this investigation.

1. Introduction

There are at least two motivations to study the magnetic behaviour of Fe/Nd multilayered thin films. First, magnetic multilayers are an interesting topic by them selves. Novel features arise unexpectedly if one deposits these new magnetic materials. Transition metal/non-magnetic metal and transition metal/rare earth metal multilayers are all underintense research worldwide. Basic research of fundamental magnetic properties as well as novel applied device-reated research, is intense activity. Second, Nd-rich phases were found in some way to be responsible for the very high coercivity of the superhard NdFeB sintered magnets. The question is: which phases form if the Nd-Fe system is deposited as a thin film multilayer which is later thermally annealed?

In sintered NdFeB magnets an annealing at 600°C was found to be essential to reach very high BH_{MAX} products. Fidler[1] was the first to report on the Nd-rich phases using EDX microanalysis in some sintered magnets. These phases were found on the grain boundaries with volume fractions around 10 percent. Earlier investigations, still completely independently of the NdFeB magnets, by Drozzina and Janus[2], Croat[3], Coey[4], Sagawa et alii.[5], found several different phases in the Nd-Fe system. Oxygen as the most obvious impurity was long thought to stabilize the Nd-rich phases, as reported by Schneider et alii.[6], Bo-Ping et alii.[7], Hadjipanayis et alii.[8] and Cabral et alii.[9]. A connection of al these works and the phases found there was established by Schneider et alii.[10]. They found two phases identified as A_1 with a Curie temperature T_C = 245°C, magnetically hard, and A_2 with T_C = 231°C, magnetically soft. Within the Nd-Fe system A_2 appears upon annealing of A_1 at 600°C. A_1 was also found by these researchers in Nd-rich NFeB. A_2 could not be found in NdFeB. Since A_1 disappears also in Nd-rich NdFeB upon annealing at 600°C these authors guess that the beneficial effect of the 600°C annealing of sintered magnets would be the gradual transformation of A_1 in $Nd_2Fe_{14}B_1$. A_2 was identified as the Nd_5Fe_{17} compound by Moreau et alii.[11]. Oxygen seemed unessential as an important impurity in these latter studies.

Research on the Nd-Fe thin film system is rapidly gaining momentum. Taylor et alii.[12] studied the magnetic properties of Nd_xFe_{1-x} and Nd_xCo_{1-x} arnorphous thin films. Sperimagnetic structures were proposed to explain the alignment of the magnetic moments in these films using Mossbauer spectroscopy, magnetometry and Hall effect measurements. Sellmyer et alii.[13] report on the relationship between magnetic properties and microstructure in thin amorphous and crystalline Fe/Nd multilayers. Hisoito et alii.[14] found Iron spin-reorientation with decreasing temperatures in Fe/Dy as well as Fe/Nd multilayers. These studies were later extended by the same group, Mibu et alii.[15], more systematically. Baczewski et alii.[16] found strong perpendicular anisotropy along with high coercive fields and remanence at cryogenic temperatures in Fe/Nd multilayers. Toukatos and Hadjipanayis[17] also found this strong increase in HC at low temperatures in sputtered amorphous NdFe thin films.

In this paper we report on the deposition of multilayered Nd/Fe thin film structures and their evolution under thermal treatment. Some Boron implanted Nd/Fe multilayers were also analyzed as deposited and under thermal treatment.

Experimental details

The Fe/Nd multilayers were prepared by sequential thermal evaporation in a Balzers UMS500 system at a base pressure of 1×10^{-8} rnbar using a dual e-gun. The multilayers were deposited on silicon oxide substrates. The total thickness of the multilayer was around 3680 with the superposition of 46 individual layers with 80 Å each. Some multilayers were implanted with 1×10^{16} ions/cm^2 at energies of 150 keV. The multilayers were submitted to a thermal annealing at 600°C in a high-vacuum furnace at pressures lower than 2×10^{-7} mbar.

In order to verify the multilayer structure and the modifications after implanation or annealing processes the samples were analyzed by Rutherford Backscattering Spectroscopy (RBS) using an alpha particle beam of 760 keV incident energy and incident and scattering angles of zero and 160°C respectively. The overall resolution of the RBS spectrometer was 12 keV. The transformation and phases formed after implantation and annealing processes were studied by Conversion Electron Mõssbauer Spectrometry (CEMS). The CEMS spectra were obtained in a backscattering geometry using a source of 57Co in a Rhodium matrix. All CEMS spectra were obtained at room temperature using a proportional counter added to a conventional constant acceleration Mõssbauer Spectrometer. In order to study the magnetic behaviour of the samples some hysteresis loops at room temperature were taken using a vibrating sample magnetorneter (VSM).

Experimental results

Fig. 1 shows the RBS spectra of the Fe/Nd samples. Fig. 1a corresponds to the as deposited sample where we can see the typical oscillations indicating the multilayer structure. Although the resolution of the RBS spectra is low, the layered structure can be seen with clarity. After annealing at 600°C a great change occurs indicating that the Nd appears to segregate to the surface of the samples *as* is shown in fig. 1b. However, it is difficult to prove this behaviour on the based on RBS only.

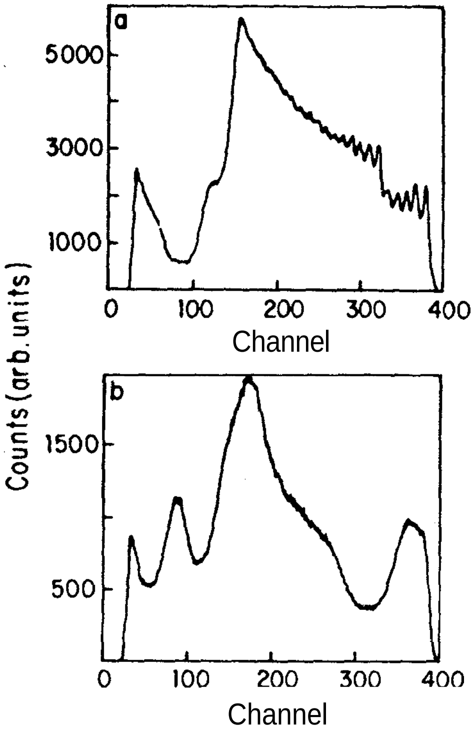

Fig. 1 – RBS spectrum of Fe/Nd rnultilayer (760 keV α particles): a) as-deposited condition and b) after annealing at 600°C during 150 min.

Fig. 2 shows the RBS spectrum of the multilayer implanted with B^+. Comparing this spectrum with the as deposited sample, fig. 1a, a very small modification in the spectrum can be noticed, due to the intermixing of some Fe/Nd at the interfaces caused by the Boron implantation. But, essentially the multilayer structure is maintained. Fig. 2b shows the RBS spectrum of the boron-implanted sample annealed at 600°C. Comparing fig. 2b with fig. 1b we see a great similarity of the two spectra, indicating that the Boron implantation has a minor effect on the interdiffuson of Nd and Fe.

Fig. 3a shows the CEMS spectrum of the asdeposited sample. As can be seen the sextet relative to a-Fe in present. Along with this sextet another sextet and a doublet can be identified in the spectrum. Unfortunately the second hyperfine

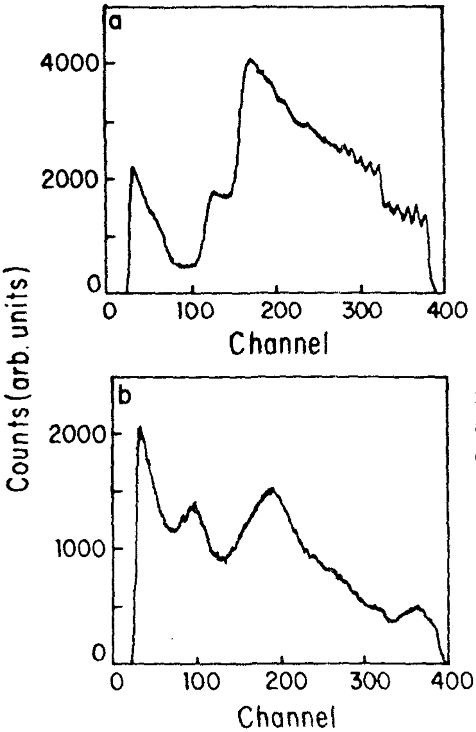

Fig. 2 - RBS spectrum of Fe/Nd multilayer implanted with (1×10^{16}) B+(ions/cm2): a) as irnplanted and b) after annealing at 600°C during 150 min.

field and the doublet could not be associated with the known Fe/Nd phases of the literature. Table 1 shows the Mossbauer fitting parameters.

Fig. 3b presents the CEMS spectrum of the sample thermally treated at 600°C. By comparing this spectrum with the spectrum of fig. 3a we can see that the area of the doublet grows, indicating a reaction between Fe and Nd which is confirmed by the RBS spectrum of fig. 1b. The new small hyperfine field of 173 kOe corresponding to another magnetic phase also can be identified. Again, we cannot associate this new phase with the known Fe/Nd phases. Table 1 shows the fitting parameters.

Fig. 4a shows the CEMS spectrum of the multilayers impianted with boron. It is noteworthy that after implantation the doublet disappears completely, while the two sextets, corresponding to the α-Fe and the other unidentified Fe/Ndphase remaín.

The CEMS spectrum of the sample implanted with Boron and annealed at

Table 1 – Mössbauer fitting paramters of samples as deposited, annealed at 600°C, boron implanted and annealed at 600°C, were AH = hyperfine field, ΔE_Q= quadrupole splitting, Is= isomer shift and Γ = line width.

Sample	AH (Koe)	ΔE_Q (mm/s)	Is(mm/s)	Γ (mm/s)	Ident
	327	0	-0.11	0.28	a-Fe
As Dep.	304	0	-0.09	0.25	?
	0	0.36	0.29	0.26	?
	330	0	-0.11	0.27	a-Fe
Anneal.	250	0	-0.0001	0.69	?
600°C	0	0.35	0.22	0.31	?
	173	0	-0.11	0.53	?
Implant.	330	0	-0.11	0.27	a-Fe
B^+	320	-0.04	-0.09	0.26	?
Implant.	332	0	-0.11	0.27	a-Fe
B^+	303	0	-0.001	0.42	?
Anneal.	0	0.47	0.24	0.59	?
600°C	167	0	-0.31	0.54	?

600°C (fig. 4b), shows some modification. Besides the two hyperfine fields appearing in fig. 4a, another small hyperfine field of 167 kOe and the original doublet appear. This spectrum can be compared with the spectrum of fig. 3b. There are differences, however. The quadrupole splitting is larger than the one of fig. 3a and the isomer shift of the small hyperfine field is different from that shown in fig. 3a, see Table 1. Another difference is that the second hyperfine field of 304 kOe that appears in the as deposited sample, fig. 3a, is present in fig. 4b, while in fig. 3b it is absent.

Fig. 5a shows the in plane hysteresis loop of the as deposited sample. The coercivity in this case is high compared to Fe thin films[18], corresponding to 204 Oe approximately. The hysteresis loop of the sample thermally treated at 600°C, fig. 5b, shows a different form, indicating the coexistence of two different noninteracting magnetic phases.

Fig. 6a shows the hysteresis loop for the sample implanted with Boron. A great reduction of the coercive field is evident as compared to the unimplanted multilayer of fig. 5a.

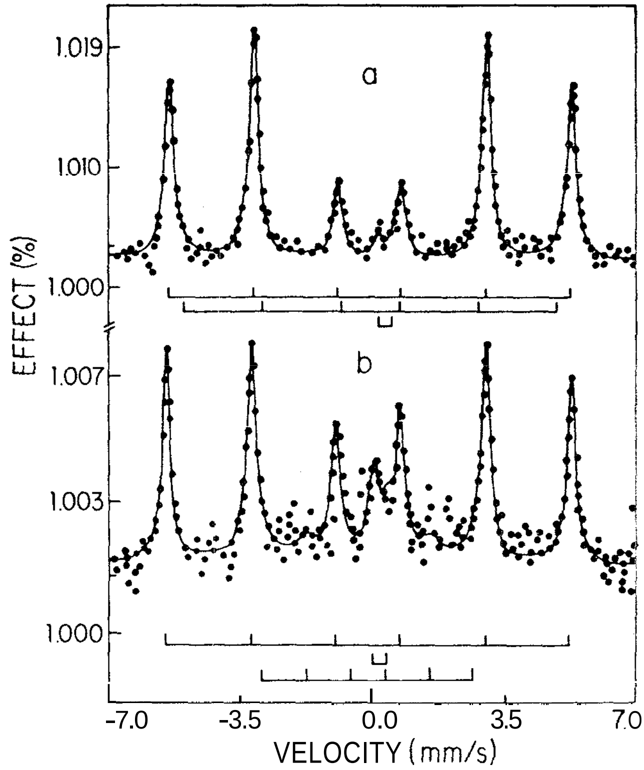

Fig. 3 – ^{57}Fe Mossbauer spectra of Fe/Nd multilayers: a) as-deposited condition and b) after annealing at 600°C during 150 min.

Fig. 6b shows the in-plane hysteresis loop of the implanted sample annealed at 600°C. Here again two different magnetic phases appear. The two coercive fields are similar to those of fig. 5b.

Discussion and Conclusions

Several qualitative trends emerge readily if one analyses the experimental results of the Fe/Nd multilayers upon annealing.

Comparing first the as deposited Fe(80)/Nd(80) sample with the available results in the literature[13] we find that the deposition at room température of Fe/Nd leads to a faint but unmistakable reaction at the interfaces, as evidenced by the Mossbauer result, fig. 3a. This is in contrast with the results of Mibu et

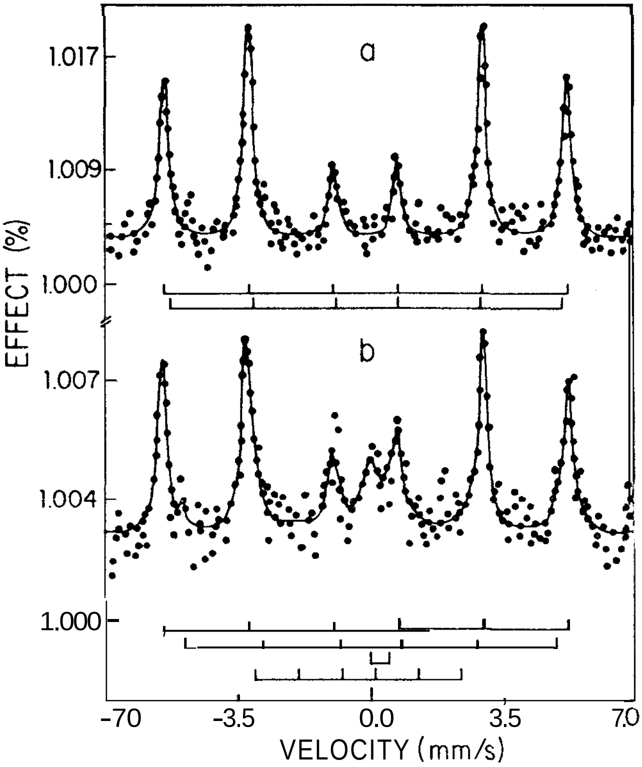

Fig. 4 – a) ^{57}Fe Mõssbauer spectrum of Fe/Nd multilayer after B^+ implantation and b) after annealing at 600°C durig 150 min.

alii.[15] who deposited the multilayer at -50°C and thus could avoid the interfacial intermixing. On the other hand we find a coercive magnetic field similar to the one found by Sellmyer et alii.[13]. This group prepared the multilayers employing a multiple-gun sputtering system. Mixtures at the interfaces are to be expected with this deposition method.

Implanting this as deposited multilayer with Boron leads to a surprising result. The RBS result, fig. 2, shows a somewhat less defined multilayer structure, which means that some intermixing is effectively produced upon implantation, but the Mõssbauer spectrum is much simpler, fig. 4a, which means that one phase produced upon deposition is effectively destoyed. Our interpretation of this result is

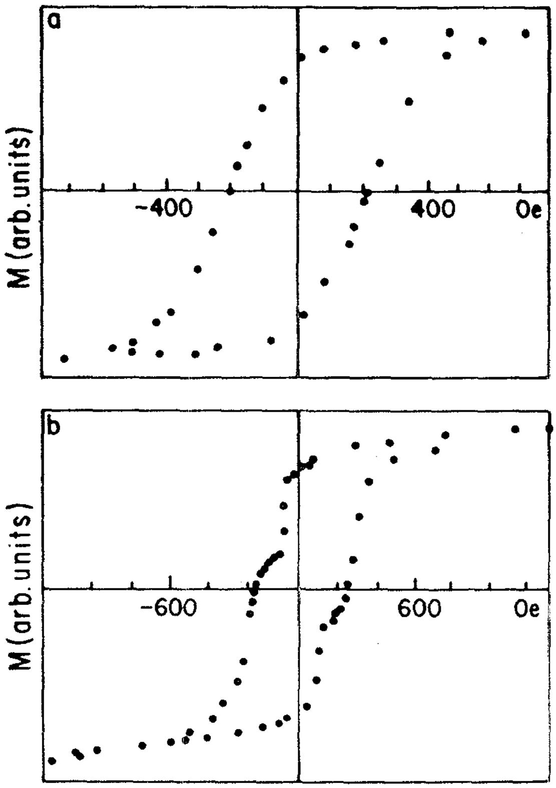

Fig. 5 - In plane hysteresis loops for Fe/Nd multilayers: a) as-deposited condition and b) after annealing at 600°C during 150 min.

that the deposition of the Fe/Nd multilayer leads to some intermixing of Fe into Nd or vice-versa with a solid solution of Nd in Fe, which in the Mossbauer result is represented by the sextet with a hyperfine field of 304.65 kOe. Some intermixing of Fe and Nd leads, however, to an unknown NdFe phase, represented in the Mossbauer spectrum by the doublet which is somehow blown up by the Boron implantation.

This interpretation is consistent with the magnetization result. In fig. 5a the coercivity is higher than one would expect from a simple picture of Fe layers separated by paramagnetic Nd. By implanting the multilayer with Boron we find a drastic reduction of the coercive field, which now is very close to the in-plane coercive field of Iron[18]. Thus the reduction of coercivity is most probably related to the annihilation of the NdFe phase upon implantation. Another interpretation based on the assumption that Boron as an sp element changes the exchange interactions within the multilayer seems less plausible to account for this coercivity reduction.

The annealing at 600°C of the multilayers leads to a strong interdiffusion and phase formation. This is clearly evidenced by all experimental results. The Mõssbauer spectra show that severa1 NdFe phases are formed. We could not identify these phases based on the known Mõssbauer results in the literature[15]. On the other hand the Mõssbauer results indicate that α-Fe is allways present after annealing. This probably means that the annealing time used in this work is too short for a complete reaction of the products. Further work is necessary to assess this information more clearly. The magnetization results of the annealed multilayers, figs. 5b and 6b, are very interesting. The interpretation we give to the hysteresis curves is that the samples are constituted of two noninteracting ferromagnetic phases after the annealing. These phases, which are similar from the magnetization standpoint, are clearly different for the unimplanted and for the Boron-implanted annealed samples if the Mõssbauer results are confronted.

This work shows for the first time the behaviour of Fe/Nd multilayers upon thermal annealing. The results, still preliminary, indicate that the Fe/Nd thin film system behaves differently to the bulk system upon annealing. Much work is necessary to clarify this subject further.

References

1. J. Fidler, IEEE Trans. Magn. 23 2106 (1987).
2. V. Drozzina and R. Janus, Nature 135, 36 (1935).
3. J.J. Croat, J. Appl. Phys. 53, 3161 (1982).
4. J.M.D. Coey, CEAM Newsletter 7, 3 (1987).
5. M. Sagawa, S. Hirosawa, H. Yamamoto, Y. Matsuura, S. Fujimura, H. Takuhara and K. Hiraja, IEEE Trans. Magn. 22, 910 (1986).

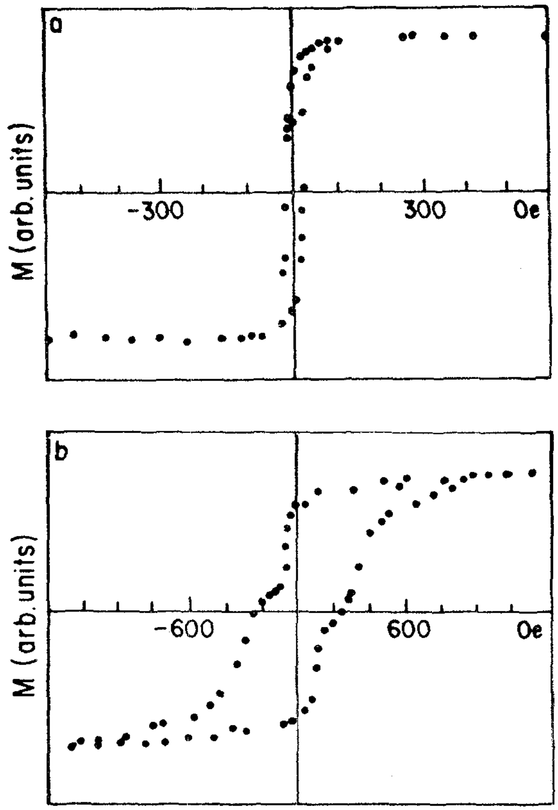

Fig. 6 - In plane hysteresis loops for Fe/Nd multilayers: a) after B^+ implantation and b) after annealing at 600°C during 150 min.

6. G. Schneider, E. Th. Hening, G. Petzow and H.H. Stadelmaier, Proceedings of 5th Int. Symp. on Magn. Anisotropy and Coercivity in Karz-Earth-Transition Metal Alloys. Bad Sodam FRG (1987) **347-362.**

7. Hu Bo-Ping, J.M.D. Coey, C.J. Cardin, E.J. Devlin and I.R. Harris, J. Less-Common Met. 144, L29 (1988).

8. G.C. Hadjipanayis, A. Tsorikatos, J. Strzeszewiski, G.J. Long and O.A. Prinsle, J. Magn. Magn. Mat. 78 L1 (1989).

9. F.A.U. Cabral, S. Gama, R.S. Turtelli and F.A.L. Machado, Proceedings 2nd Seminário sobre Materiais Magnéticos (Assoc. Bras. Metais, São Paulo).

10. A. Schneider, F.J.G. Landgrat and F.P. Missell, J. Less-Common Met. 153, **169 (1989).** G. Schneider, F.J.G. Landgrat, V. Villas-Boas, G.H. Bezerra, F.P. Missell, A.E. Ray, to be published.

11. J.M. Moreau, L. Paccard, J.P. Nozieres, F.P. Missell, G. Schneider and V. Villas-Boas, to be published.

12. R.C. Taylor, T.R. McGuire, J.M.D. Coey and A.. Gangulee, J. Appl. Phys. **49, 2885 (1978).**

13. D.J. Sellmyer, Z.R. Zhao, Z.S. Sham and Natis, J. Appl. Phys. 61, **4323** (1987).

14. N. Hosoito, **K.** Yoden, K. Mibu and T. Shinjo, **J.** Phys. **C8-1777.**

15. K. Mibu, N. Hosoito and T. Shinjo, J. Phys. Soc. Japan 58 **2916 (1989).**

16. L.T. Baczewiski, M. Plecuch, J. Durand, G. Marchal and P. Delcroix, Acta Phys. Pol. A76, **357 (1989).**

17. A. Tsoukatos and G.C. Hadjipanayis, J. Appl. Phys. 67, **5728** (1990).

18. D.H. Mosca, P.H. Dionisio, W.H. Schreiner and I.J.R. Baumvol, to be published.

Resumo

O comportamento magnético de multicamadas Fe/Nd como depositada e após tratamento térmico é apresentado neste trabalho. As amostras foram analisadas por CEMS e VSM. Os resultados indicam forte interdifusão e formação de fases envolvendo Fe e Nd. A identificação destas fases não pôde ser feita utilizando o diagrama de fase para o sistema Fe-Nd. Amostras implantadas com boro também são analisadas neste trabalho. Resultados preliminares são apresentados.