OCCUPANCY OF 4*d*-STATES IN T (T: Mo, Nb) FROM NEXAFS $L_{3,2}$ SPECTRA OF Nd-Fe-B-T ALLOYS

V. Bilovol*, F. D. Saccone

Universidad de Buenos Aires,
Av. Paseo Colón 850, C1063ACV, Buenos Aires, Argentina; e-mail: vbilovol@fi.uba.ar

Samples of $Nd_yFe_{(86-y-x)}B_{14}T_x$ (T: Mo, Nb; x = 2, 4; y = 7, 8) alloys were studied by X-ray absorption spectroscopy. The NEXAFS spectra of NdFeB ribbons produced by the melt spinning technique (as quenched, AQ) and subsequently annealed (TT) were taken at Mo and Nb $L_{3,2}$-edge. We calculated the variations in occupancy of the 4d-states (in both additives), finding an opposite trend in their filling. The most significant changes were observed in the T_2Nd_7 system, for which the electron occupancy in the 4d levels was modified to an excess of 1 electron/atom (after thermal treatment). The correlation between these results and magnetic features of the alloys are evidenced.

Keywords: *Nd-Fe-B based magnets, additive, electron occupancy.*

ЗАСЕЛЕННОСТЬ 4*d*-СОСТОЯНИЙ В Mo, Nb НА ОСНОВАНИИ АНАЛИЗА ТОНКОЙ СТРУКТУРЫ РЕНТГЕНОВСКИХ СПЕКТРОВ ПОГЛОЩЕНИЯ СПЛАВОВ Nd-Fe-B-T (T: Mo, Nb) ВБЛИЗИ ГРАНИЦЫ $L_{3,2}$

V. Bilovol*, F. D. Saccone

УДК 543.427:54-19

Университет Буэнос-Айреса, Аргентина,
C1063ACV, Буэнос-Айрес, Пасео Колон, 850; e-mail: vbilovol@fi.uba.ar

(Поступила 13 июня 2013)

Сплавы $Nd_yFe_{(86-y-x)}B_{14}T_x$ (T: Mo, Nb; x = 2, 4; y = 7, 8) изучены методом рентгеновской абсорбционной спектроскопии. Образцы имели форму полосок, полученных методом вытягивания из расплава (в состоянии после закалки), а затем отожженных. Тонкая структура рентгеновских спектров поглощения сплавов NdFeB исследована вблизи границы $L_{3,2}$ Mo и Nb. Рассчитаны изменения заселенности 4d-состояний (в обеих примесях) и обнаружены противоположные тенденции в их заполнении. Наиболее существенные изменения наблюдались в системе T_2Nd_7, где заселенность 4d-уровня изменялась более чем на 1 электрон/атом (после термообработки). Корреляция между этими результатами и магнитными характеристиками исследованных сплавов очевидна.

Ключевые слова: *магниты на основе Nd-Fe-B, добавка, заселенность состояния.*

Introduction. Neodymium-iron-boron nanocomposite permanent magnets were developed in the early 1990s [1, 2]. Their low neodymium content, less than the stoichiometric amount of 12 at.%, made them cheaper and more corrosion resistant. Moreover, their higher boron content improves the amorphization ability. These systems, called exchange-spring magnets, exhibit interesting magnetic properties due to the exchange coupling between the hard and soft magnetic phases at nanoscale. The coexistence of both types of magnetic phases results in remanence and magnetic energy product ($(BH)_{max}$) enhancement. However, the presence of the soft phases reduces the coercivity. The use of alloying components such as Mn, Cu, Nb, Ti, and Mo, among others, helps to control the grain growth during the melt-spinning production of these kind of magnets, improving in this way the magnetic response of the material [3–5]. In particular, the addition of Mo and Nb was reported to be very effective for grain refinement of nanocomposites, leading to the improvement of the coercivity after annealing [6]. However, the mechanisms that cause the suppression of α-Fe formation are not fully understood, as well as the role of Mo or Nb as an additive component that helps to stabilize the $Nd_2Fe_{14}B$ phase (φ-phase). Urse et al. explained the coercivity enhancement by the pinning of domain walls at grain boundaries where the additive precipitates, in the case of Mo-doped Nd-Fe-B thin films [7]. For Nb-doped ribbons, it was found that a higher concentration of this additive

is required than in the case of Mo in order to obtain higher coercivities and $(BH)_{max}$ [8]. Thus, a study of the electronic state of these elements becomes appropriate to elucidate the role they play as additives in Nd-Fe-B magnets. Synchrotron radiation is a powerful tool that helps in this study. The information on the electronic structure of occupied/unoccupied 4*d*-electron states in these alloys was derived from near-edge X-ray absorption fine structure (NEXAFS) measurements.

The purpose of the present work is to quantify, by X-ray absorption spectroscopy, variations in occupancy of the 4*d*-states of molybdenum and niobium added to NdFeB alloys produced by the melt spinning technique, both as quenched (AQ) and subsequently annealed (TT), and to identify correlations between these results and magnetic features of the alloys.

Experimental. The starting ingots with nominal compositions of $Nd_yFe_{(86-y-x)}B_{14}T_x$ (T: Mo, Nb; $x = 2, 4$; $y = 7, 8$) were prepared by arc melting of pure elements in argon atmosphere. The ribbons were produced by rapid solidification of molten alloy (melt-spinning) with a roll speed of 20 m/s. Ribbons were sealed in quartz ampoules in a protective atmosphere of argon. Then, the overquenched ribbons were annealed at 973 K for 20 min. The thickness of the ribbons was about 20 μm. From here, the samples are identified by their x and y values, namely, T_xNd_y (T: Mo, Nb).

The measurements (fluorescence mode) were carried out at the SXS beamline (source: D04A bending magnet) of the Laboratorio Nacional de Luz Sincrotrón, Campinas, Brazil. X-ray absorption data were analyzed using standards procedures: a linear background was fitted at the pre-edge region and then subtracted from the entire spectrum; the jump of the spectrum was normalized to unity with the post-edge asymptotic value by using a quadratic fit. All these procedures were performed using Athena software (version 0.8.056).

Results and discussion. Observed "white line" peaks, when a solid is irradiated by monochromatic X-ray photons, are the characteristic L_3 and L_2 absorption edges of an atom under research. These white lines originate from excitations of the 2*p* electrons to unoccupied *d*-states about an atom. It was showed that variations in normalized white line intensities could be used to determine changes in the occupancies of the associated 4*d*-states [9]. Then the change in the normalized white line intensity from the experimental data should be first evaluated. The width of the normalization window was chosen to be 50 eV and positioned 50 eV after the L_3 absorption edge of Nb (Mo) [9].

In this way, the normalized white line intensity ($\Delta I'_{4d}$) is determined from the intensity difference between the reference spectrum and other spectra in the regions from 2367 to 2377 eV and from 2462 to 2472 eV for the Nb series (2519 to 2529 eV and 2622 to 2632 eV for the Mo series) divided by the integrated intensity in the normalization window from 2372 to 2422 eV for the Nb series (2572 to 2622 eV for the Mo series). The $\Delta I'_{4d}$ values were also divided by the matrix-element factor of 0.0729 (Nb) or 0.0851 (Mo) and it was taking into account that $\delta n_{4d} = (-1/1.4)\Delta I'_{4d}$ (in accordance with [9]). Then by this procedure, quantification in the variation of the 4*d*-state occupancy (in electron/atom) can be obtained.

If the reference $L_{3,2}$ spectra of metallic Mo and Nb are not available, the observed variations can be referred to a known spectrum of the set. This prevents us from concluding about possible charge transfer. However, some partial trends can be analyzed regarding the role of the additive in the modification of the electronic structure of neighbor atoms. With this in mind, we decided to take as reference the spectra of AQ T_2Nd_7 samples in order to estimate variations in filling the 4*d*-states when the contents of neodymium or the additive element have been changed as well as the synthesis condition.

For Mo, the $L_{3,2}$-edge spectrum obtained from the TT Mo_2Nd_7 sample exhibits lower-intensity white lines (Fig. 1a), as compared to AQ Mo_2Nd_7 (used as reference), indicating that some electrons occupy the Mo 4*d*-states after the sample has been submitted to thermal treatment. The difference in the 4*d* occupancy in these samples was calculated to be nearly 1.1 electron/atom (see Fig. 2). Similar features were observed for other Mo-containing

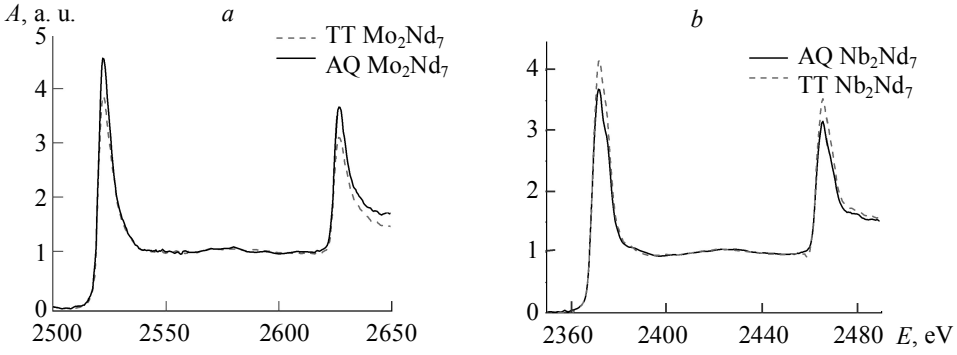

Fig. 1. Mo (a) and Nb (b) $L_{3,2}$ absorption edge for AQ and TT Mo_2Nd_7.

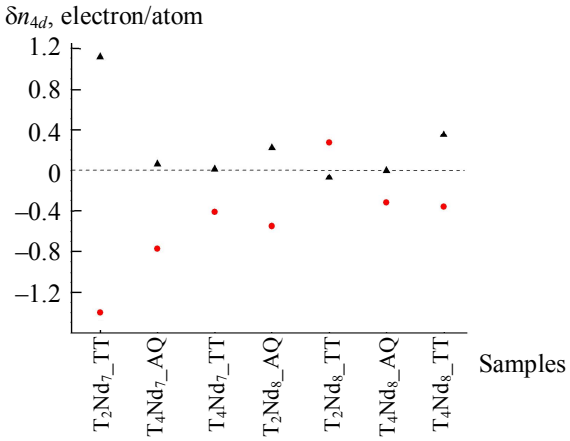

Fig. 2. Variations in 4*d* states for Mo (▲) and Nb (●) doped NdFeB alloys taking as a reference AQ T_2Nd_7 spectrum (T: Mo, Nb).

samples (although to a lesser extent). The spectrum obtained from the TT Nb_2Nd_7 sample (Fig. 1b) exhibits higher-intensity white lines as compared to the AQ Nb_2Nd_7 one, indicating that some electrons have left the Nb 4*d*-states after the thermal treatment procedure. The difference in the 4*d* occupancy in these samples was calculated to be nearly –1.4 electron/atom (Fig. 2). Similar features were observed for other Nb-containing samples (although to a lesser extent). As can be seen, the calculations show the opposite trends in filling the 4*d*-states for Mo and Nb. This could be an indication of the acceptor nature (Mo) or donor nature (Nb) of the refractory elements in NdFeB alloys. It is remarkable that the only exception was observed for the same concentration of the elements in thermally treated samples: TT T_2Nd_8 (T: Mo, Nb). Another interesting observation is that, in general, the variations in the 4*d*-states of Nb are more significant than in Mo. This fact is an indication that the 4*d* orbitals of Nb are more affected than the Mo ones when the sub-bands of the additive elements added to NdFeB alloys are considered.

Some interesting conclusions can be made from Fig. 2 about how thermal treatment influences 4*d* occupancy of the as-quenched samples. For instance, for the AQ T_2Nd_7-TT T_2Nd_7 (T: Mo, Nb) pair, thermal treatment leads to an enhancement of the 4*d* occupancy in Mo (as was mentioned), while it diminishes in Nb. For the AQ T_4Nd_7-TT T_4Nd_7 (T: Mo, Nb) pair, the scenario is different: thermal treatment favors 4*d*-state filling in Nb, but not in Mo (almost unchangeable). For the AQ T_2Nd_8-TT T_2Nd_8 (T: Mo, Nb) pair, when Mo is added, 4*d* filling is promoted, while Nb addition is unfavorable for the occupancy of the 4*d*-states. When the AQ T_4Nd_8-TT T_4Nd_8 pair is analyzed, it is observed that in Mo thermal treatment favors filling of the 4*d*-states, while no appreciable changes were observed in the Nb case. From these remarks, it seems that more relevant variations in the 4*d*-state occupancy come from the alloys containing 2 at.% of the additive elements (both Mo and Nb) after the AQ samples have been subjected to thermal treatment. XRD analysis revealed a considerable amount (~45 %) of the metastable $Nd_2Fe_{23}B_3$ phase in both Mo_2Nd_7 and Nb_2Nd_7 TT samples [8]. The unit cell volume of this magnetic phase is slightly larger than the corresponding to $Nd_2Fe_{14}B$, but it has 224 atoms per cell instead of just 68 atoms (as in this latter phase), meaning that the free volume of the cell of the $Nd_2Fe_{23}B_3$ phase is smaller due to higher atomic density [10, 11]. The large differences in δn_{4d} observed for T_2Nd_7 could be attributed to a preferable dilution of the T atoms in the $Nd_2Fe_{14}B$ structure and low precipitation of T-rich phases at grain boundaries (for which variations in δn_{4d}, depending on T and Nd concentrations are not expected). For the other samples studied in this work, the dilution preference seems to be reduced but should not be ruled out. This fact could originate in a higher amount of precipitates of Mo or Nb in grain boundaries.

A comparison between the variation in occupancy of the 4*d*-states in the refractory element and the magnetic properties of Nb-doped samples is shown in Fig. 3. It is observed that larger variations in the Nb 4*d* electronic levels match with the maxima in magnetic saturation (which is an indication of the moment of Fe atoms in Bohr magneton units). As can be concluded from this figure, regardless of whether an electron is gained or lost in this electronic band, the exchange coupling must be altered, which causes an enhancement of the Fe magnetic moment.

Summarizing, the electronic structure of Mo and Nb atoms used as additive elements (in low concentration) in Nd-Fe-B alloys shows variations that are the direct manifestation of different occupancies of the 4*d* states in molybdenum and niobium. The variations are of different nature in these elements. The 4*d*-bands of both atoms are sensitive to changes in Nd concentration and/or conditions of samples synthesis.

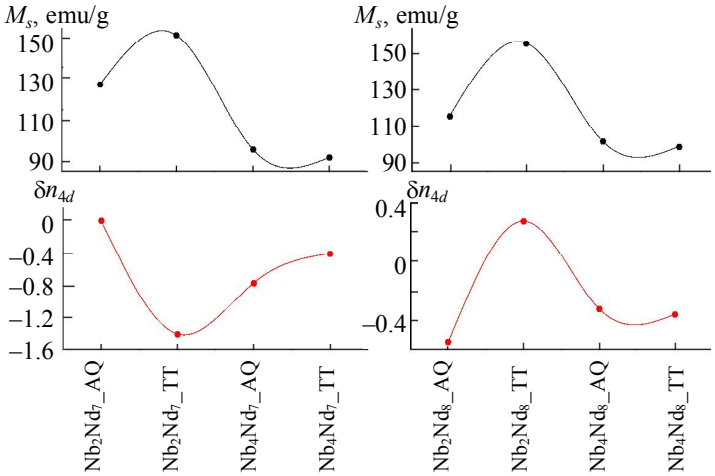

Fig. 3. Magnetization saturation and δn_{4d} data for each Nd-doped sample. The lines serve as a visual guide.

Conclusion. NEXAFS spectra at Mo and Nb $L_{3,2}$-edges were analyzed. From the differences in the normalized white line intensities, the variations in occupancy of the 4*d*-states in Mo and Nb in the Nd-Fe-B-T (T: Mo, Nb) alloys were determined. Two opposite trends in filling the orbitals were observed: predominantly more occupied bands in Mo and less occupied in Nb with respect to the corresponding reference data. The occupancy variation is slightly higher for Nb. Thermal treatment of AQ samples containing 2 at.% of the additive elements induces more significant variations in occupancy of the 4*d*-states, quantified as 1.1 and –1.4 electrons/atom in Mo and Nb, respectively. This can be attributed to a preferable dilution of T atoms in the φ-phase rather than the presence of Mo or Nb precipitates at grain boundaries. The presence of a large amount of the $Nd_2Fe_{23}B_3$ phase indicates that the chemical potential is clearly modified for the lowest content of Nd and T atoms analyzed in this work, this being the origin of the higher T-dilution. On the other hand, a clear correlation between the magnetic saturation of the samples with the occupation degree of the 4*d*-states in the refractory atoms was found.

Acknowledgment. We acknowledge partial financial support from Argentine Agencies (CONICET and ANPCYT), as well as support by LNLS (Project SXS 13498), Campinas–SP, Brazil. We appreciate the help of E.J. Lede in the measurements.

REFERENCES

1. T. Schrefl, J. Fiddler, and H. Kronmuller, *Phys. Rev. B*, **49**, 6100 (1994).
2. G. Hertzer, *IEEE Trans. Magn.*, **26**, 1397 (1990).
3. M. Spyra, D. Derewnicka, and M. Leonowicz, *Phys. Status Solidi (a)*, **207**, No. 5, 1170–1173 (2010).
4. M. Leonowicz, M. Spyra, and E. Jezierska, *AIP Conf. Proc.*, **1347**, 103 (2011).
5. I. Betancourt and H. A. Davies, *J. Iron Steel Res. Int.*, **13**, No. 1, 146 (2006).
6. M. Leonowicz, M. Spyra, and E. Jezierska, *Mech. Adv. Mater. Struct.*, **18**, No. 3, 181–184 (2011).
7. M. Urse, M. Grigoras, N. Lupu, and H. Chiriac, *J. Phys.: Conf. Ser.*, **303**, No. 1, 012009 (2011).
8. V. Bilovol, S. Ferrari, L. G. Pampillo, D. Derewnicka, M. Spyra, and F. D. Saccone, *IEEE Trans. Magn.*, **49**, No 8, 4622–4625 (2013).
9. D. H. Pearson, C. C. Ahn, and B. Fultz, *Phys. Rev. B*, **47**, No. 14, 8471–8478 (1993).
10. K. H. J. Buschow, D. B. de Mooj and H. M. van Noort, *J. Less-Common Met.*, **125**, 135 (1986).
11. A. Nino, T. Nagase, and Y. Umakoshi, *Mater. Trans.*, **47**, No. 2, 335–340 (2006).