

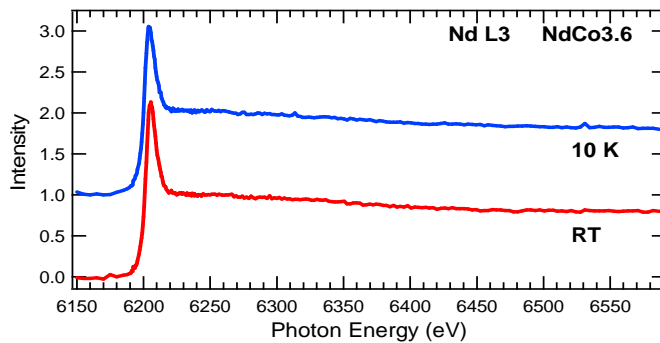
## **The Perpendicular Magnetic Anisotropy of amorphous NdCo thin films studied by EXAFS using linearly polarized X-rays**

NdCo thin films, 100 nm thick, of two different compositions and deposition conditions were analyzed by X-ray absorption spectroscopy at the Nd  $L_3$  and Co K edges to understand the origin of their perpendicular magnetic anisotropy. The composition of the samples was NdCo<sub>3.6</sub> (22% at. of Nd) and NdCo<sub>4.6</sub> (19% at. of Nd). The alloys were prepared by two methods: co-sputtering and alternated sputtering (AS). The last deposition mode, AS, created a modulation in composition Co/Nd in the direction normal to the substrate in a way similar to a multilayer, although the Nd layer did not complete an atomic monolayer in any of the compositions of the analyzed alloys. The films deposited by this method (AS) had a higher PMA than the films prepared by co-sputtering with the same atomic concentrations. The spectra were taken at normal and glancing incidence, and at RT and LT (10 K). The Nd  $L_3$  spectra measured at both orientations and temperatures did not detect EXAFS oscillations. In correspondence, Co EXAFS spectra were well fitted using only Co scatters. The apparent reason behind this is the large distance between Nd and next neighbours, longer than the second shell in Co, and the static disorder in the film. A dichroism effect was observed in the Nd  $L_3$  and Co K spectra. The Nd  $L_3$  white line was more intense at normal incidence in any of the measured samples. The difference in intensity was stronger, of about 10%, in the samples with higher Nd concentration (NdCo<sub>3.6</sub>), and of about 2.5% in NdCo<sub>4.6</sub> films. The Co-Co coordination was about 5% larger in the plane than out of the plane in any of the samples. Second and third Co neighbours were detected at fcc positions, suggesting the presence of segregated Co what it would indicate that the concentration of Co atoms per Nd at the Nd sites could be below the nominal Co concentration. A thermal expansion anomaly was detected in all the samples. The Co-Co bond length increased at low temperature, being the highest increase observed in the NdCo<sub>3.6</sub> films ( $\Delta l/l=1.7\%$ ). This negative thermal expansion (NTE) was anisotropic. The homogeneous samples, which had a lower PMA, had a larger NTE in the direction perpendicular to the plane of the sample, whereas the modulated samples, with higher PMA, had a higher NTE in the direction of the plane of the sample. The NTE is the only structural parameter that could be linked to the magnetic properties of the film. Its anisotropy might explain the origin of the PMA in these samples

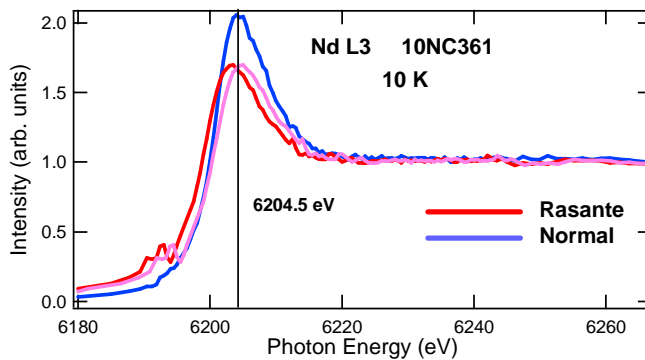
### **Results**

Figure 1 shows the EXAFS spectra of NdCo<sub>3.6</sub> at the Nd  $L_3$  absorption edge taken at RT and at 10 K. It evidences the lack of EXAFS oscillations in the spectra, showing that Nd atomic environments were as disordered as in an atomic gas.

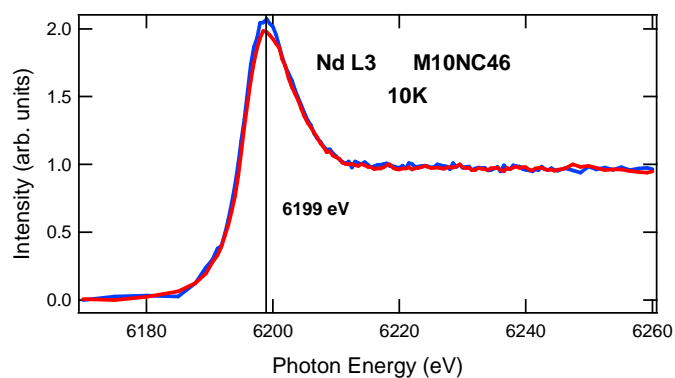
Figure 2 shows the difference in intensity in the white line of the Nd L3 spectra of  $\text{NdCo}_{3.6}$  taken at normal and glancing incidence. There was also a downward shift of about 1 eV of the spectrum taken at glancing incidence. There was a shift of about 1 eV downwards from the spectra taken at RT to the spectra taken at 10 K. These shifts must be confirmed by XPS. Figure 3 shows that such a dichroism was not significant in the  $\text{NdCo}_{4.6}$  films. Figure 4 shows the dichroism in the Co K edge between normal and glancing incidence, similar in all the samples. Figure 5 shows the quality of the fits using Co scatters only assuming second neighbours in an fcc structure. Finally, the panel in figure 6 summarizes all the results from the analysis of all the spectra: change in the Nd L3 white line intensity, Co coordination and Co-Co bond length with respect to x-ray beam incidence, sample temperature, Co concentration and type of film deposition (co-sputtering and AS).



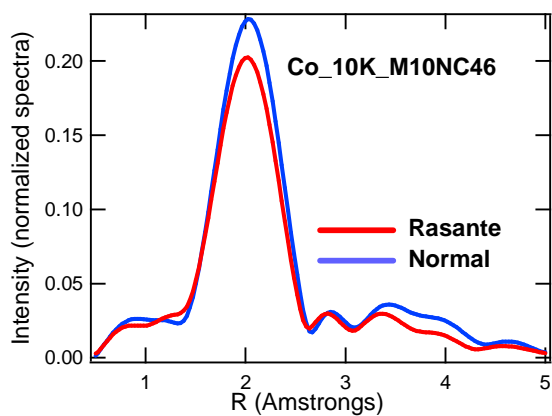
**Figure 1.** Nd L3 EXAFS spectra of  $\text{NdCo}_{3.6}$  taken at 10 K and at RT.



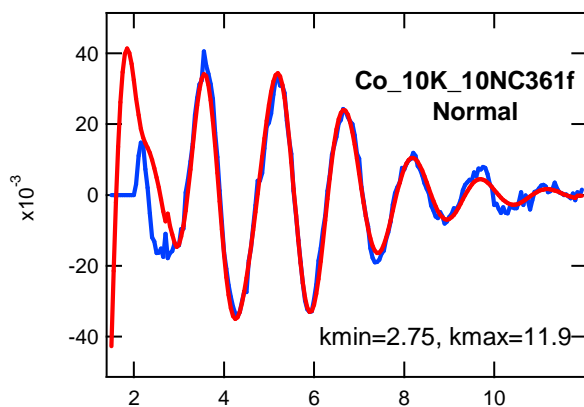
**Figure 2.** Nd L3 EXAFS spectra of  $\text{NdCo}_{3.6}$  taken at 10 K at normal and glancing incidence. The spectrum in pink color is the same as the taken at glancing incidence but shifted 1 eV upwards.



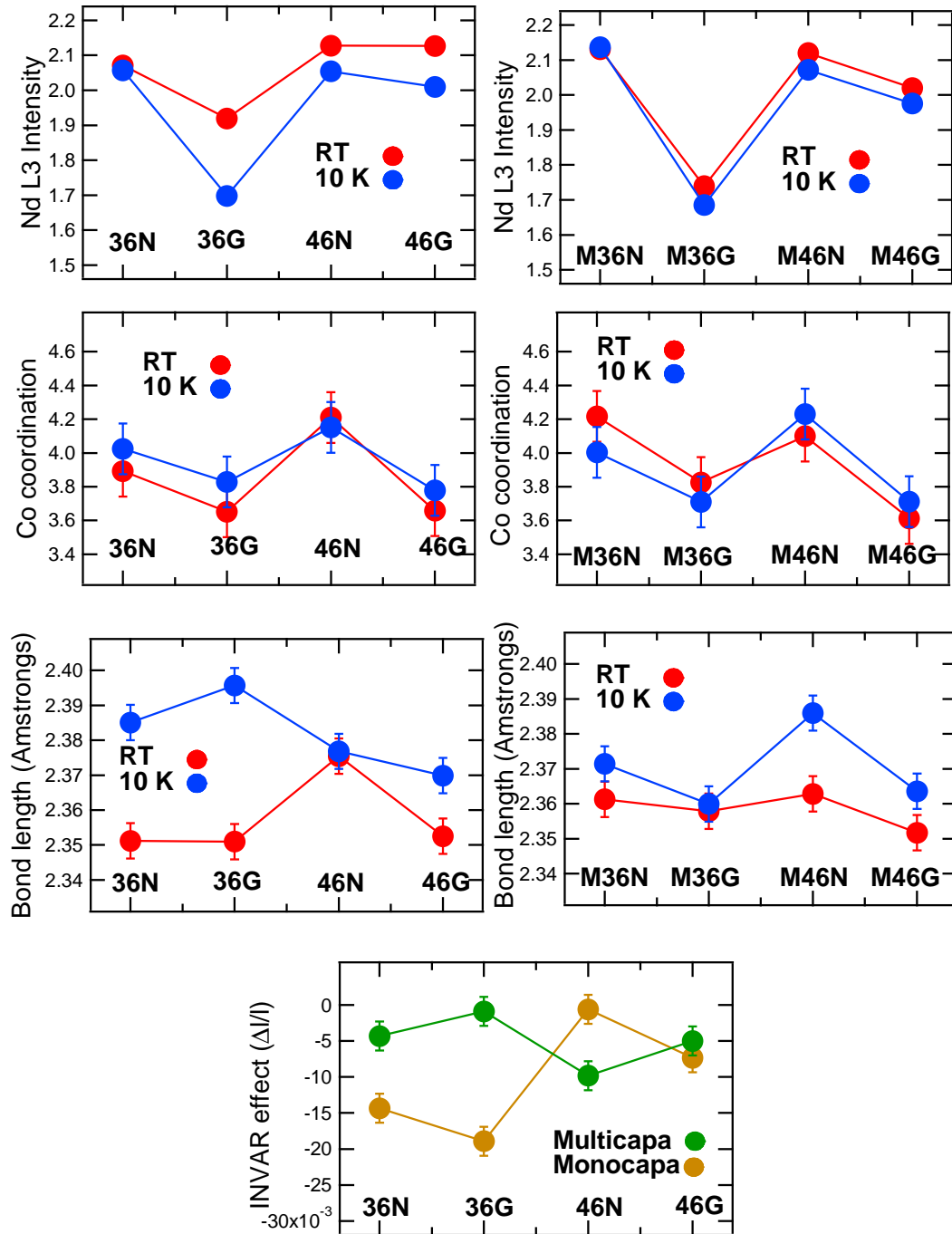
**Figure 3.** Nd L3 EXAFS spectra of  $\text{NdCo}_{4.6}$  taken at 10 K at normal (blue) and glancing (red) incidence.



**Figure 4.** Co K EXAFS spectra (R-space) of AS-deposited  $\text{NdCo}_{4.6}$  taken at 10 K at normal (blue) and glancing (red) incidence.



**Figure 5.** Co K EXAFS spectra (k-space) of  $\text{NdCo}_{3.6}$  taken at 10 K at normal (blue) incidence and its fit (red line) using only Co scatterers at fcc sites up to the third shell.



**Figure 6.** Parameters obtained from the analysis of the spectra: Nd L3 white line intensity, Co coordination, Co-Co bond length and invar effect. The numbers 36 and 46 correspond to the relative concentration of Co respect to Nd. The letter M means Multilayer. N is for normal incidence and G is for glancing incidence. Normal incidence proves bonds in the plane of the film.

## Discussion

The Co coordination was always higher at normal incidence than at glancing incidence in any of the films investigated, indicating that the number of Co neighbours was larger in the plane of the films than perpendicular to it. The difference in coordination between both orientations was similar in all the cases, of about 10%. It was slightly higher in the films with less Nd concentration, which were also the ones with higher PMA energy. But this could be due to the difference in Co concentration between both alloys. Co coordination was of about 4 at first neighbours, significantly smaller than the expected, since fcc-Co has 12 first neighbours. This coordination value might not be the real one and it was quenched in the EXAFS spectra likely due to static disorder. The asymmetry in coordination is similar to the observed in TbFe films and it was interpreted as an asymmetry in the distribution of TM-TM and RE-TM pairs, which has served to justify the PMA observed in these kind of amorphous magnetic alloys (ref. 1). As in the case of the TbFe films, the asymmetry in Co coordination can be interpreted as a large number of Co-Co pairs in the plane than out of the plain.

It is not possible to give Nd-Nd or Nd-Co coordinations or bond length distances from the Nd EXAFS spectra because their EXAFS amplitude was negligible. This is likely due to the intrinsic static disorder in the films and the expected large bond length between Nd atoms and between Nd and Co atoms. The Nd-Co and Nd-Nd interatomic distances in NdCo<sub>5</sub> are 2.90 and 3.97 Å respectively. They are similar to the second and third neighbours distances detected in Co, whose contribution to the EXAFS signal in Co were significantly small due to static disorder.

One of the main observations is the surprisingly small Co-Co bond length, of about 2.36 Å, when compared with the Co bond length in fcc-Co, which is of 2.51 Å. This could be caused by an asymmetric atom distribution. However, that is not the case here. The best model that fitted the Co K edge EXAFS spectra included second and third neighbours. The relative coordination and interatomic distances of these other two shells with respect to the first shell showed that Co atoms retained an fcc structure. These other shells were largely more disordered than the first shell with a Debye-Waller factor  $\sigma^2$  which doubled, or triplicate in the case of the third shell, the Debye-Waller factor  $\sigma^2$  found in the first shell. The contraction in bond length can be produced by defects in the lattice or by the formation of grains of very small size. It is known that in low dimensional systems there is a decrease in bond length (ref. 2,3,4). Bond length shrinking can be also caused by Nd: Co-Co bond length in NdCo<sub>5</sub> is 2.459 Å, smaller than in fcc-Co. According to the Bethe-Slater curve, the Co magnetic moment should decrease when the bond length is reduced. However, this is not always the case since the magnetic moment of Co in bulk is substantially quenched, and it is higher in clusters and clean surfaces than in bulk. MDC results showed that Co

moments were not too different from Co bulk, even they had higher magnetic moments. Then, probably the contraction in bond length of Co is not caused by a compressive strain in the film but by a Co network with plenty of defects. The average coordination of Co is actually about three times smaller than the expected in fcc Co.

Another important observation is that the Co sublattice had an apparent negative thermal expansion (NTE): Co-Co bond length was smaller at RT than at 10 K. These variations in Co bond length were larger in the films with lower Co concentration. This NTE was anisotropic, i.e., bond length variation was different in the normal than in the parallel direction to the plane of the sample. The samples with modulated concentration were the ones with higher PMA. Their NTE was larger in the parallel direction than in the normal. It was just the opposite in the non-modulated samples. The size of the thermal expansion was relatively high: in between 1.5 % and 0.8 %. There is no record, to our knowledge, of such a strong anomalous thermal expansion in Co. However, for the same range of temperature, crystalline NdCo<sub>5</sub> has an anomalous thermal expansion in the c-axis of the unit cell which is compensated by a contraction in the a-axis. This effect was similar but stronger in PrCo<sub>5</sub> (ref. 5). In crystalline NdCo<sub>5</sub> and PrCo<sub>5</sub> the anisotropy below RT is dominated by the RE (much more in the case of NdCo<sub>5</sub>) which reorientates the magnetic easy axis to the basal plane (a-axis), perpendicular to the c-axis, which is the orientation of the magnetic anisotropy of the Co sublattice (ref. 6). This is what might be happening in this case. The observed expansion of the Co sublattice at low temperature might be induced by the expansion of the Nd sublattice, assuming that the anomalous thermal expansion found in the films was due to magnetic interactions. This is because MCD done in similar films showed that the magnetic moment of Nd was the only significantly enhanced at low temperature with respect to RT, whereas the magnetic moment of Co remained practically constant.

MCD also showed that the PMA of these films was caused by the Nd sublattice. Assuming that the observed NTE was linked to the magnetism in the analyzed alloys, it can be deduced a correlation between their PMA energy and their NTE. The stronger NTE was found in the homogeneous alloy with the higher Nd concentration. However, their PMA was lower than in the modulated film of the same Nd concentration. This can be explained by observing that the NTE is stronger in the plane for the modulated sample (with higher PMA energy) than out of the plane, where in the homogeneous sample (with lower PMA energy) is just the opposite. The same explanation works for the samples with lower Nd concentration. Actually, the sample with higher NTE in the plane of the sample had the highest PMA. The PMA in these films can be understood taken as a reference the behaviour of the magnetic anisotropy in crystalline NdCo<sub>5</sub>. In this crystal there is a competition between the anisotropy of the Co and Nd sublattices, with their easy axis direction perpendicular to each other. At low temperatures, the anisotropy of the Nd sublattice overcomes that of Co at the same time that the c-axis,

which is the one where the distance between Nd is the smallest, does not shrink as expected, but remains constant or increases. Although Nd-Nd interatomic distances were not possible to be measured in these films, the anisotropy found in the distribution of Co-Co pairs in the plane and out of the plane indicates that Nd-Nd distance was shorter in the plane than out of plane. The increased concentration in Co in the modulated films increased the distance between Nd-Nd pairs in the direction out of plane, as it happens in crystalline NdCo<sub>5</sub> if the a-axis was oriented out of the plane. It is interesting to notice that the epitaxial growth of NdCo<sub>5</sub> has been possible only with the a-axis oriented out of the plane and the c-axis parallel to the plane (ref. 7). If it is assumed that the amorphous alloys try to relax to the atomic environment of their crystalline counterpart (ref.8), we might conclude that the analyzed alloys approached the NdCo<sub>5</sub> crystalline structure with a preference of their c-axis in the plane, explaining the resulting PMA.

Although no information was possible to extract from the Nd EXAFS spectra, Nd XANES showed some. The Nd L3 white line was more intense in normal incidence than in glancing incidence. The anisotropic effect was the largest, of about 20%, in the films with higher Nd concentration. For the same concentration, the modulated samples had a slightly large effect than the homogeneous, whose PMA energy was smaller. The anisotropic effect was almost negligible in the homogeneous sample and of about 5% in the modulated film, the one with the highest PMA energy. The variations in intensity with temperature were larger in the homogeneous samples, and almost negligible in the modulated samples. The samples with less Nd concentration had the highest PMA energy. But they also had the highest magnetic moment of the Co sublattice. The variations in the Nd white line can be then interpreted as caused by the large chemical interaction between Nd and Co, since Co lost its magnetic moment in these alloys mainly by hybridization of their 3d orbital with the 5d orbitals of Nd.

## Conclusions

X-ray absorption spectroscopy at the Nd L3 and Co K edges showed the presence of structural anisotropies in NdCo amorphous thin films with PMA. It was detected a negative thermal expansion in the Co matrix of all the films which is likely linked to the magnetic properties of the alloys. The films with the higher PMA have a larger NTE in the direction parallel to the film.

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