# X-ray imaging and spectroscopy of single antiferromagnetic NiO nanoparticles

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NiO nanoparticles (NP) exhibit relevant physical features when compared to the bulk materials, such as charge-transfer effects and interesting antiferromagnetic (AF) spin structure. Chemical and magnetic studies are often limited to ensembles of NiO NP which are limited to averaging their individual electronic, and magnetic properties with respect to their individual characteristics. In this work, we have analyzed with single-particle sensitivity the chemical, and magnetic properties of three samples of NiO nanoparticles in a size range of 40-60 nm, synthesized by wet chemistry routes, by means of synchrotron-based X-ray Photoemission Electron Microscopy (X-PEEM) combined with X-ray Magnetic Linear Dichroism (XMLD) around the Ni  $L_{3,2}$  edges. The analysis of the local X-ray absorption spectra indicates a strong dependence of the oxidation state of the individual NP with the oxidation protocol of each sample. Furthermore, first evaluation of the XMLD signal with respect to the linear polarization angle, a signature of AF order, indicates different AF spin easy axis orientations between individual NiO NP.

# I. INTRODUCTION

Attention in nanoscale magnets has recently increased due to their unique and different properties and behaviours compared to bulk scale. Transitional metal oxide nanomaterials are specially interesting because of their great applicability and possibility in the technological sector, extending from catalysis of chemical agents to biomedical applications [1]. In 1961, Néel suggested that NiO nanoparticles (NP) manifested a slight ferromagnetism or superparamagnetism behaviour. This latter one has been assumed to be related to an uncompensated number of spins on a two antiferromagnetic (AF) sublattice model [2]. Nonetheless, Kodama et al [3] suggested that sometimes the NiO behaviour is not understandable under this premise and it could be understood as a more complicated sublattice structure resulting from finite size effects, in which a change in the magnetic order due to the reduction of the coordination of surface spins is induced. This study remains experimentally inconclusive, as most of the experimental work has been limited to groups of particles, and therefore, to averaging the properties of individual nanoparticles in the ensembles. In this situation, single NP characteristics are hidden by the collective behaviour of the ensemble, so a deeper insight must be performed in individual NiO NP to characterize their intrinsic properties regarding morphology, size, chemical composition and magnetic response. Consequently, both an appropriate synthesis method and an advanced characterization toolbox must be chosen as means to have a good control over size, chemical composition and structure. Moreover, the understanding of the AF origin of NiO NP requires a deep chemical and magnetic characterization through the analysis of data with statistical significance to establish unequivocal conclusions.

In this work, we report on a thorough image processing and analysis of chemical and magnetic data with single particle sensitivity from several tens of NiO NP, obtained from combining synchrotron-based X-ray Photoemission Electron Microscopy (X-PEEM) with X-ray Magnetic Linear Dichroism (XMLD).

## II. EXPERIMENTAL METHOD

## A. Sample preparation

Highly diluted dispersions of NiO NP with sizes ranging around 40 to 60 nm were prepared by wet chemical routes at the Magnetic Nanomaterials Group, University of Barcelona, and dispersed onto Si wafers with lithographic markers. To avoid charging and increase the signal-to-noise ratio from the NP in the X-PEEM experiments, a thin carbon film was deposited onto the substrates. The samples were prepared in three steps. Step 1: Ni NP were obtained by the thermal decomposition of Ni(acac)2 in 1-octadecene using oleic acid as surfactant agent. Step 2: Ni was oxidized to NiO by heating up to 350°C for 48 h in atmospheric conditions. Step 3: for the X-PEEM experiments, NP monolayers of the samples were prepared by drop casting in atmospheric conditions of highly diluted NP suspensions.

Sample A follows the protocol above described. For Sample B, a second oxidation process was performed after step 3 consisting in heating at  $525^{\circ}$ C for 12 h in atmospheric conditions. For sample C, an additional thermal treatment was performed after step 2 consisting in heating up to 700°C for 72 h in atmospheric conditions.

## B. X-ray absorption spectroscopy of single NP

The analysis is based on X-PEEM mesurements of the samples collected in two different synchrotons (Swiss Light Source and Helmholtz-Zentrum Berlin - BESSY) by various members of the Magnetic Nanomaterials Group. The three samples were brought under an acquisition process of X-ray Absorption Spectroscopy (XAS). This was performed to obtain XMLD information, which is the difference between spectra taken with vertical and horizontal linearly polarized light. The existence of XMLD contains information of magnetic ordering, as it is sensible to the AF spin axis orientation. Two stacks for every sample were obtained, understanding stacks as a collection of images containing the particles. The procedure consisted of recording sequences of X-PEEM images using different linearly-polarized light and scanning the photon energy around the Ni  $L_{3,2}$  edges. For sample A, for each polarization XAS was repeated twice to have more statistics. For sample B, just one image stack per light polarization was performed. Representative examples of elemental-contrast X-PEEM images from samples A and B are shown in Fig. 1. For Sample C, in addition to local X-ray absorption spectra (not shown in the following), measurements of the XMLD contrast at fixed energy values (869,2 eV and 870,4 eV) around the  $L_2$ multiplets as a function of the electric field (E) vector angle of the linearly polarized light was performed with E-vector angles of  $15^{\circ}$ ,  $30^{\circ}$ ,  $45^{\circ}$ ,  $60^{\circ}$ ,  $75^{\circ}$  and  $90^{\circ}$ . In this case, a large number of images with a high exposure time were acquired and averaged to gather statistics. One stack was obtained for each polarization. From this study we aimed to determine if the dependency of XMLD signal with respect to the incident X-rays follows the usual proportionality to the square of the magnetic moment  $\langle M^2 \rangle$ .

### III. DATA ANALYSIS

### A. Analysis of the local X-ray Absorption Spectra

The first step in extracting the whole spectra was the alignment between all images in the stack for every energy using an Image J routine [4]. Although applying this correction, drifts below two pixels in x-axis and yaxis showed up and could not be corrected. A larger accuracy in correction was impossible due to the small elemental contrast difference between the particle and the background signal, remarkable for the smallest dots. This might introduce some inaccuracies in the results, and its effects will be discussed later. Thereupon, a background correction was needed due to non-similar emission and absorption characteristics of the different background zones. To overcome this issue, an *Image J* routine called *Sliding Paraboloid* was used and the improvement was evident. Next step was the selection of the particles with boxes of different sizes that adapted to the largeness of the particles with the intention of getting the biggest and cleanest signal possible. It is crucial to avoid including any background in the selected area, as it will average down the overall signal from the particle. The local spectra, such as those obtained in Figs. 2 and 3, are obtained by extracting the mean intensity of each box for every energy and dividing it by the background signal. The background of every particle is measured with the same box dimensions close to the particle for each energy, trying to avoid possible halos. Further details of the process on which this analysis is based is given in [5]. In Sample B, the X-ray local spectra showed a monotonically decaying absorption with increasing energy due to different possible reasons, such as a small signal of the NP, current decay and self-irradiation effects (see an example of this in the Annex A). These artefacts are not unusual in XASbased measurements. To correct this slope, a polynomial fit was applied for each spectrum masking the peak energies and subtracting it to the original one (see Fig. 5 in the Annex A).

All particles in the provided samples were analyzed with square and rectangular areas of either  $2 \times 2$  or  $2 \times 1$ pixels depending on their size. Almost all particles were well analyzed, except the smallest dots (1 px). Some astigmatism effect is presented as asymmetrical halos, more evident for the largest dots. Notice that the lateral spatial resolution of X-PEEM is low, of the order of about 30 nm, so the box size may not refer to the actual size, but apparent, as the XAS just indicates the regions where the electrons are emitted.

In sample A, a total of 100 particles were selected, whereas in sample B only 10 were analyzed. The number of particles analyzed are enough to hold conclusive chemical results, even more than in other particle-by-particle measurements techniques, such as high resolution TEM.



FIG. 1: Elemental contrast X-PEEM images measured with linear polarization (a) from sample A at 853.7 eV and (b) sample B at 853.5 eV, taken with a field of view of 50  $\mu m$ . Position of the analyzed particles are marked with circles. (b): Due to second oxidation process, particles seem to be embedded.

The sample A spectra was scaled conveniently to 0 at the pre-edge  $L_3$  and to 1 at the post-edge  $L_2$ , but sample B presented flat parts of the spectra around the zero due to slope correction, and the same normalization could not be applied. The scatter plots in Fig. 2 show examples of normalized local XAS spectra from illustrative particles in samples A and B.

For Sample C, a similar alignment was applied, but in this case the X-PEEM image stack manifested a diffraction pattern and some astigmatism for the different linear polarization angles which could not be fully corrected. The absorption signal was extracted for each linear polarization angle for 36 particles from areas with similar sizes as mentioned above, and it was divided by the background to enhance the signal. The box shape of the latter

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was "freehand" instead of square or rectangular.

To quantify the amount of metallic Ni and NiO present in selected individual particles within samples A and B, the local isotropic XAS spectra (sum of horizontal and vertical polarization) were fitted to a weighted linear combination of reference bulk spectra of Ni and NiO taken from [6]. Further details of the process on which this analysis is based is given in [7]. Lastly, a criterion was developed to ascertain the percentage of each phase, taking into consideration different typical spectral characteristics of each chemical phase and making a compromise between them to achieve the best feasible conclusion. Because of the large number of particles and spectra, all the criteria were not applicable the same way for each one, so a percentage of uncertainty must be taken into consideration.

#### B. X-ray Linear Dichroism (XMLD) data

XMLD signal was obtained by making the difference between the outcome signal of the two different polarization stacks. Therefore, knowing a priori that XMLD shows up around the Ni  $L_{3,2}$  edges [6], it was fundamental that both spectra overlapped out of these edges. The background signal was measured with boxes of different shapes and sizes, and located at various distances from the particle in order to associate an error bar to the XMLD signal. It was expected to obtain an XMLD signal at the L edge given by [8]

$$I = I_0 + I_1 \cdot \cos^2(\alpha). \tag{1}$$

Where  $I_0$  and  $I_1$  are constants and  $\alpha$  is the angle between the polarization vector and the easy direction of the AF moment. A python code was developed, to make the analysis of a large number of particles easier [9].

#### IV. RESULTS

#### A. Analysis of the isotropic XAS spectra

Representative examples of the outcome spectra are shown in Fig. 2 (a) (I) and (II) for sample A and (b) for sample B. We can distinguish two main peaks in Ni and NiO phases named as  $L_3$  (~ 853 eV) and L2 (~ 871 eV) in the absorption spectra referenced above. A signature of NiO phase is the edge splitting effect in  $L_{3,2}$ peaks. In  $L_3$  a shoulder (855.3 ± 0.1 eV) is manifested, whereas in  $L_2$  a double peak is perceived. The main reason for this difference is because Ni only has two final states in XAS transitions, in contrast to NiO, which has more allowed transitions between initial and final states (so-called multiplet effects).

Considering the spectral characteristics of each species, a criterion was well thought out. We considered the  $L_{3,2}$ shapes, mainly the  $L_2$  splitting, and the distances between the main peaks. This distance was computed using the position of A edge instead of the average energy



FIG. 2: Normalized XAS spectra (dots) from illustrative particles of sample A and B compared to the best weighted fits from the Ni and NiO standards (black lines). The analyzed particles are indicated with green and pink circles, respectively in Fig. 1. (a): The spectrum (I) belongs to a large particle, where a clean signal came out, meanwhile spectrum (II) was from a smaller one and presented more noise. This could hide magnetic information. (b): The A and B edges from the spectrum are more visible and evidence the NiO content, although  $L_3$  edge is smaller than expected.

of A and B, because B was barely noticeable for most particles (see Fig. 2). Besides that,  $L_{2,A}$  position is fixed and very similar for both specimens, therefore, it is a good reference. We obtained from the reference spectra a distance of  $17.4 \pm 0.3$  eV for NiO and  $17.8 \pm 0.2$  eV for Ni. Secondary, the ratio  $L_{2,3}$  and  $L_{2A,2B}$  peaks were taken into consideration.

Particles of sample A turned out to be rather pure Ni. All particles had around 90% to 100% a chemical composition of Ni. Taking into account the described criterion, it was not easy to reach a conclusion about the uncertainty but considering a 5% appeared to work with all the results. Although the small presence of a shoulder in  $L_3$  is typical of NiO, it was clear the little oxide content due to the non-edge-splitting  $L_2$  peak, as indicated in Fig. 2 (a). However, for some particles, we could appreciate a small double-ledge in  $L_2$ , pointing out that some oxide phase was contained, like the spectrum (a) (I). The mean distance for the particles between  $L_3$ and  $L_{2,A}$  was  $17.3 \pm 0.4$  eV, which was compatible with

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both phases, slightly more consistent with NiO. On the other hand, a valley between peaks and a small signal ratio  $L_3: L_2$  was a common feature among all the spectra. For this high determined percentage of Ni, it was expected to find a flat area with a higher intensity value, but a valley that resembled NiO shape at these energies was obtained. However, these two described spectral features were attributed to charging effects [10], and it was concluded that the absence of the splitting was a more determining fact. With spectrum (a)(II) in Fig. 2 we can illustrate the importance of analysis procedure, as noise is appreciated and could mask some features like the double peak in  $L_2$ . Here, we cannot completely assure if the particle is less oxide than others because of the drift and the box size consequences, remarked at the previous section, or whether it is truly Ni.

Sample B turned out to be more oxidized. It is straightforward the NiO content on account of the shape of  $L_2$  peak. Paying attention to  $L_3$  height, we can see that the ratio  $L_3: L_{2A}$  was smaller than expected likely due to charging effects. The mean distance between peaks was  $17.4 \pm 0.4$ , which is compatible with both phases. As these spectra had to be corrected for the decaying absorption with energy, the flat areas at the pre-edge  $L_3$ , the post-edge  $L_2$ , and between these two edges may be artificially enhanced and thus, do not fit so well with the reference spectra at these zones. Charging effects in the sample could also lead to higher intensity values, like in the  $L_3$  shoulder. Despite this, we focused in the  $L_2$  shape and concluded that particles had between 15% and 30% of metallic Ni, with an uncertainty of 12%. The fitting and the sample spectra do not seem to match perfectly (more noticeable for sample A), mainly because of height difference between the reference and the sample peaks. This does not affect our analysis, since here we only focus on relative differences in spectral of shape and proportionality, and not in quantifying the number of 2p to 3d transitions associated to the X-ray absorption process.

## B. Analysisi of XMLD spectra

The XMLD results for sample A, shown in Fig. 3 (a) and (b), are consistent with what was found in the isotropic XAS analysis. As the particles are mostly pure Ni, XMLD is mostly insensitive to its ferromagnetic phase, so it is reasonable that spectra taken with both polarizations are almost identical. However, particles with a higher content of NiO, showed up some asymmetries for the  $L_3$  and  $L_2$  peaks. When normalizing to the isotropic signal, the noise was enhanced, and this was caused by pre-edge normalization that produced a fluctuation signal near to 0 at the pre-edge normalization at a value above 0 was performed in order to characterize the XMLD magnitude and obtained values between 2% and 10%. However, the spectrum did not overlap so well.

For sample B, an illustrative spectrum is shown in Fig.

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FIG. 3: (a) and (c): Comparison of XAS spectra of the different polarization of the particles circled in pink in Fig. 1. (b) and (d): XMLD obtained by subtracting the polarized signals in order achieve the referenced signal [11] shown at the top-right, for sample A and B respectively. As it is observed in sample B, the signal is very small.

3 (b). Whereas the isotropic XAS analysis indicated a predominance of the NiO phase, the outcome spectra were highly influenced by charging and current decay effects. This resulted in noticeable noise and broadening and narrowing of the XMLD signal, therefore, no conclusive XMLD was found in any particle out of the 10 analyzed. Moreover, the polynomial correction of the XAS spectra, mentioned before, did not help, as the spectra could not be properly normalized. The XMLD difference without isotropic normalization obtained ranged between 0,05 to 0,15 in arb. units.

We must consider that all these analyzed NP have a very small signal, difficult to treat and normalize properly, as they are analyzed with very small size boxes. We have to take into account the small XMLD even for bulk material (<10%). Knowing the aimed shape of XMLD spectrum, shown in Fig. 3 (b) and (d), it was established that the best attainable spectrum was subtracting the polarized signals. In addition, we cannot exclude the possibility of existing groups of nanocrystal grains with different AF axis orientation that may interfere with the results, since we would obtain an averaged signal and magnetic information would be hidden.

#### 1. XMLD contrast vs. linear polarization angle

For sample C, the evolution of the XMLD signal as a function of the electric field vector angle of the linear polarization was measured, Fig. 4 shows XMLD contrast as a function of the E-vector angle for three selected individual NP together with their respective fits to Eq. (1),



FIG. 4: XMLD signal of three particles in  $L_2$  edge (~ 870 eV) from sample C as a function of the E-vector angle. X-PEEM images from the corresponding particles are shown at the left for each spectra, where the background box shape is outlined in green. The spectra has been fitted to Eq. (1) (red line) in ranges of  $\alpha \in [90^\circ, 180^\circ]$  for (a),  $\alpha \in [135^\circ, 225^\circ]$  for (b) and  $\alpha \in [0^\circ, 90^\circ]$  for (c).

for different  $\alpha$  angles between the E-vector and the AF axis. While preliminary and not quantitative yet, our data seem to be compatible with the observation of three NP with different orientations of the AF easy axis, shifted 45° (b) and 90° (c) with respect to the orientation of the NP shown in (a). At room temperature, NiO is an antiferromagnetic material characterized for a fcc structure and a slight rhombohedral deformation along one of the four [111] directions. This leads to the formation of four possible twin domains in NiO bulk. This type of domain possesses a sixfold degenerate magnetic state within the easy plane. Our results seem thus apparently consistent with the observation of some of these orientations.

Over the 36 analyzed particles around 28% had a tendency like (a), 42% like (b) and 30% like (c). Percentages are consistent with what was expected, as the AF axis orientation could take any of the three possible orientations. It should be noted that these results are limited to the in plane projection, and a complete study would require collecting similar data at selected azimuthal angles to unequivocally determine the AF spin axis orientation.

## V. CONCLUSIONS

We have performed a thorough analysis of the chemical and magnetic properties of individual NiO NP of about 40-60 nm in size, from three different samples, prepared by wet chemical methods. The data were extracted from images and local spectra obtained by the combination of X-ray Photoemission Electron Microscopy and the X- ray Magnetic Linear Dichroism effect. The small signal and the presence of some X-PEEM artefacts related to charging have been a challenge to achieve unequivocal conclusion. Even so, the analysis of the isotropic local Xray absorption spectra shows a strong dependence of the oxidation state of the individual NP with the oxidation protocol of each sample. While sample A shows a prevalence of the metallic Ni phase, samples B and C show a predominance of the NiO phase. Moreover, the evolution of the XMLD contrast at the Ni  $L_2$  edge with respect to the linear polarization angle appears to be reasonable with the observation of different AF spin easy axis orientations between individual NiO NP. However, a deeper magnetic and chemical characterization is still required to better understand single NiO NP behaviour.

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# VI. ANNEX

## A. Polynomial fit to correct the monotonically decaying absorption with increasing energy from NiO NP local XAS spectra

The decaying absorption with energy of the X-ray local spectra from the particles was corrected by fitting a polynomial fit masking the peak energies. The best fit for the set of data was established by using the least squares method. The corrected spectra was obtained by subtracting the raw spectra by the fit.



FIG. 5: Representative normalized XAS spectrum from sample C. The raw spectrum is shown at the inset together with the polynomial fit (black line) used for normalization.