Harwell, 22nd August 2024

Evaluation of PhD thesis written by **Marianna Gerina.**

Title of the thesis: **Preparation and characterisation of magnetoelectric core@shell nanoparticles**

The title of the thesis describes very well the objective: the synthesis and characterisation of core-shell nanoparticles with magnetoelectric properties. While there are few single phase magnetoelectric materials, they suffer from weak magnetoelectric couple. In order to improve the coupling a common strategy is to produce composite materials, where the different phases give the material the desired properties. One of the multiple properties of nanomaterials is the great increase of the surface to volume ration, making very appealing to produce core-shell nanoparticles with magnetoelectric coupling.

The thesis is well written and structured, following the required quality for publication in peer reviewed journals, as it is demonstrated by the publication of three papers where the candidate was an author (including one as first author). The thesis starts with a general introduction to different relevant topics. In the first section of Chapter 1 the main concepts of magnetism required for the development of the objectives of the thesis are presented. The main characterisation technique (Small Angle Neutron Scattering, SANS) is presented in its own section. The final objective of the thesis is to produce multifunctional materials which are described in the last section of Chapter 1. Chapter 2 describes accurately all the experimental methods used by the candidates to characterise the materials (although I'm missing a description of the experimental methods used for the synthesis of the nanoparticles). The bulk of the thesis is Chapter 3, where the main results obtained during the thesis are presented and analysed. It is formed by six sections, one per material studied. It is relevant to remark that the first three have been already published in peer-reviewed indexed journals and another one has been submitted to publication, demonstrating the quality of the work done. I would like to commend the quality of the samples produced, which allows a deep characterisation using advance techniques not only using laboratory techniques, but large facilities too. The characterisation techniques have been wisely chosen in order to obtain the required information about the systems and the data analysis is sound and robust. The results and knowledge gained during the work have been used in order to decide the next steps in order to finally produce a magnetoelectric core-shell nanoparticle system. Chapter 4 list the main conclusions obtained during the thesis and finally chapter 5 list all the bibliography used for the work. The bibliography list all the relevant references on the field and demonstrates that the candidate is up to date with the state of the art on the research on magnetic/magnetoelectric nanoparticles.

In the next section I will ask all my questions to the candidate:

- What is the physical property that governs the coercivity of a magnet?
- Do you think that the shape anisotropy plays a role in bulk magnets? Why?
- Is Eq. 1.11 valid for a pellet of powdered nanoparticle?
- Is there any angular dependence on the magnetic SANS signal? If so, is it helpful or detrimental in any way?
- What conditions are needed for a nice transfer between the strain and the piezoelectricity in a composite material? (for example between $CoFe_2O_4$ and $BaTiO_3$)
- What wavelength did you used for the SAXS experiments? Why?
- Does Fig. 3.2 show the total averaged scattering or just a sector of the detector?
- How the demagnetisation factor change with the size of a magnetic object?
- How the M_z values extracted from the SANS data analysis compare with the ones extracted by magnetisation measurements?
- Do you have any hypothesis that might explain why nanocubes have a higher SAR than nanospheres?
- Is Figure 3.7 data normalised by the sample mass or the magnetic material mass? If it is the former, could you estimate the normalisation by magnetic mass so there could be a more direct comparison between the different panels?
- What parameters are fitted with the LOA model?
- Extracting information from Fig. 3.18 is certainly challenging. Have you used any method to try to avoid biases when selecting the nanoparticles?
- Do you have any hypothesis explaining why only the sample Co23Mn77 has a $\Delta M>0$
- Does the Mn-Co substitution only affect the surface anisotropy or do you expect changes in more physical parameters?
- How much sample is synthesised per batch of $CoFe_2O_4$@$BaTiO_3$? Could you think of experimental techniques that you could use to investigate the sample if you have decided to study the sample CF@BT2?
- In Chapter 3.6 you show a big correlation between the match of the crystallite size obtained by XRD and SAS (and hence the lack of structural disorder) with the lack of magnetic disorder. Does this mean that the contribution from the surface anisotropy to the magnetic disorder on nanoparticles is negligible?

- How the magnetisation results (ZFC/FC and hysteresis curves) compare between the $CoFe_2O_4$ cores and the nanocubes?
- What is the difference between the sample CS10 and CS38/CS39?
- Why $NiFe_2O_4$ and $CoFe_2O_4$ are indistinguishable for X-rays but not for neutrons?

I recommend this thesis for defense.

Dr. Diego Alba Venero, ISIS neutron and muon source