

Getting the most out of neutron powder diffraction - Revealing the microstructure evolution during sintering of magnetic nano-particles using parametric refinement

Frederik H. Gjorup¹, Mathias Mørch¹, Jakob V. Ahlburg, Jennifer Hölscher & Mogens Christensen¹

¹Department of Chemistry and Interdisciplinary Nanoscience Center (iNANO), Aarhus University, Langelandsgade 140, 8000 Aarhus C, Denmark.

fgjorup@chem.au.dk.

Nano-structuring is a crucial step in optimizing permanent magnet materials, where both the size and morphology of the individual particles heavily affect the properties of the compacted bulk magnet. The size is tuned to ensure magnetic single-domain particles, which is crucial for optimizing the *coercivity* of the magnet (the field strength required to flip the magnetic orientation), as this is lowered by the mobility of walls between domains. Generally, the minimum required *coercivity* of a permanent magnet is half of the saturation magnetization, at which point the *remanence* (the magnetization at zero field) is the limiting factor. The *remanence*, in turn, is primarily tuned by the alignment of the particles, i.e. the texture of the bulk magnet.

One way to control the alignment is through the morphology of the nano-particles, as the right particle shape leads the powder to self-alignment during compaction and sintering into dense pellets, thus optimizing the alignment of the magnetic domains in the resulting bulk magnet^[1].

The overall figure-of-merit for permanent magnets is evaluated from the volume-weighted *energy product* (a.k.a. the BH_{max}), reported in kJ/m³ (MGOe in cgs-units). It follows that the density of the final bulk magnet is an important parameter, which again is correlated with the particle microstructure. The combination of crystallite size, texture, and density emphasizes the compaction process when going from powder to bulk, which also often includes a sintering step. Powder diffraction is a powerful technique for studying the compaction and sintering processes, as proper refinement of the data can provide valuable information about phases, crystallite size, texture, and, in the case of neutron diffraction, the magnetic moments, as they develop during the compact. Neutron powder diffraction also comes with the benefit of a large probing volume, which is useful for studying bulk behavior.

The rapid improvements in both detectors and sources allow for faster and faster data collection, but the accompanying large data quantities require robust and efficient data treatment strategies. One such strategy is sequential refinement, where each pattern in the dataset is refined one after the other (typically) in chronological order, using the final model of the previous refinement as a starting model for the next.

Taking it a step further gives us parametric refinement. Here, a single overall model is used to describe an entire dataset simultaneously, while still allowing some individuality between patterns. This is accomplished by describing suitable parameters using functions or constraints across all N patterns. In this way, the remaining unconstrained parameters are allowed to more freely refine towards physically sensible minima. As an example, a given phase formation might be known to follow a certain kinetic model, and so the scale factor can be parameterized to follow that model. Likewise, the unit cell parameters for a compound known to exhibit linear thermal expansion might be described by two parameters (slope and intercept), rather than N times unit cell parameters. This is clearly a significant reduction in the total number of refined parameters, especially for large *in situ* datasets. The ability to refine across several patterns makes parametric refinement a powerful tool for disentangling correlating parameters such as intensity-dependent parameters or peak profile parameters, as it allows us to impose physically meaningful time-dependent constraints.

Using parametric refinements allows us to get the most out of our neutron powder diffraction data!

[1] Stingaciu, Marian, et al. "Optimization of magnetic properties in fast consolidated SrFe₁₂O₁₉ nanocrystallites." *RSC advances* 9.23 (2019): 12968-12976.

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