
DREAM INSTRUMENT FIRST SCIENCE

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1. SCOPE

This document outlines the plan for the first science at the DREAM instrument. It is a living document that will be updated to reflect new scientific cases, as well as the most recent developments in the sample environment and power ramp-up plan for ESS.

2. INTRODUCTION

The first science experiments on DREAM will be focused on neutron powder diffraction experiments, while the experiments for pair-distribution function (PDF) and polarized small-angle scattering (SANS) experiments have secondary priority, according to STAP recommendations in October 2023 [1]. The first science ideas suggested by the DREAM team and STAP members are incorporated. Some of the inputs can be found in [1] in their original version.

3. CALIBRATION MEASUREMENTS

This is the first type of experiment to be conducted at DREAM when the neutron beam is available. We plan to measure neutron powder diffraction standards, PDF standards, known single-crystals and samples to test polarized SANS capability of the instruments. These studies will be carried out at low, medium and high-resolution chopper settings to provide instrument resolution function for each setting. The 2D Rietveld resolution function will be obtained as well, which will help the planning of more challenging experiments. The beamline characterization studies require minimum sample environment. The results will be published in the instrument paper.

The samples include NIST Si and LaB₆ powders, Y₃Fe₅O₁₂, Cu, and Al single-crystals, NAC (Na₂Al₂Ca₃F₁₄), vanadium rods and silica spheres (for SANS resolution function).

4. INITIAL EXPERIMENTS

These measurements can be considered as a proof-of-principle of producing publishable output for DREAM during the early days. Most of the samples can be obtained from commercial vendors in large quantities. The measurements can be done with a minimum sample environment at room or liquid nitrogen temperatures.

4.1. Transition metal monoxides

Well-studied magnetic oxides with structural sublattices and relatively high ordering temperatures offer the opportunity to explore the high-resolution capability of DREAM and cover one of the focus science areas – magnetism.

The bulk NiO and nanoparticles show rhombohedral distortion at 300 K. The associated peak splitting was not resolved by the high-resolution POWGEN beamline at SNS, while it was an early science highlight for the HRPD instrument at ISIS. Other samples include MnO (T_N = 120 K), FeO (200 K) and CoO (290 K).

4.2. Zeolites and MOFs

The zeolite materials with large unit cells are another focus area for the DREAM instrument. Zeolite MFI (SiO₂ silicate-type) with the cell parameters $a = 19.90 \text{ \AA}$, $b = 20.04 \text{ \AA}$, $c = 13.38 \text{ \AA}$ (for high-resolution mode). The deuterated MOF MIL-53(Al), (Co)MOF-74-1 and (Co)MOF-74-2 (collaboration with ESS Deuteration Lab), and RE-Fe-B magnets, will be measured at room temperature to demonstrate the refinement of complex structures from neutron powder diffraction data.

4.3. Electrode materials in pristine state

New types of electrode materials that recently showed great potential in applications, can be measured with neutrons to define their crystal structure. For example, Li₂Ni₂W₂O₉ is a new compound that was recently synthesized and its structure was solved [5]. A number of analogous compounds Li₂M₂W₂O₉ with M=Zn, Co, Fe, Mn... can be synthesized, with similar properties but unknown crystal structures.

5. MORE CHALLENGING EXPERIMENTS

More challenging experiments include smaller samples that have to be synthesized. The sample environment and data reduction shall be geared towards in-situ studies at low and high temperatures.

5.1. Perovskites and complex oxides

Obvious examples include variable temperature studies of materials showing structural and/or magnetic transitions, e.g., Fe₂O₃ (Morin transition at 260 K), perovskites CaTiO₃, LaCrO₃ (T_N = 280 K), and Co₃O₄ (T_N=40 K). The in-situ neutron powder diffraction studies of A more challenging but possibly high impact result may come out of Fe₃O₄ measurements over a wide temperature range from below Verwey transition (120 K) to above Curie (T_c = 860 K) temperatures [2], focusing on subtle changes around these transitions. The cubic and spherical Fe₃O₄ nanoparticles with reduced critical temperatures will be studied with additional PDF and polarized SANS measurements.

5.2. Small samples with cation disorder

AA'BB'O₆ double-double perovskites (DDP) are good test cases and constitute a potential source of results that would be obtained on novel materials. Previously, 50-100 mg samples of cation-ordered perovskites were obtained from high-pressure synthesis (6-8 hours data collection on the WISH instrument at ISIS). Their structures are tetragonal ($P4_2/n$, a , $c \approx 7.5 \text{ \AA}$) with some cation inversion disorder and their Curie temperatures vary from 10 to 500 K. Most of these materials have simple $k = (000)$ ferrimagnetic structures, e.g. CaCuFeReO₆ (T_c = 500 K) [3], but some have more complex spin structures; CaMnCoWO₆ has an unusual combination of commensurate and incommensurate spin orders (Mn-site $k = (0.5 \ 0.5 \ 0.5)$ and Co-site $k = (0.5 \ 0.42 \ 0.5)$), below T_c = 18 K [4]. Newly synthesized DDP compositions will be provided for DREAM commissioning by STAP members.

5.3. Hydrogen-containing samples

H-containing samples; metal hydroxides, hydroxy salts, small organics, perhaps a MOF. The hydrogen evolution reaction (HER), oxygen evolution reaction (OER), and CO₂ reduction catalysts: in this field, copper-based compounds, alloys, and borides/carbides can be studied with powder diffraction and PDF on DREAM, to define the crystal structure and influence of microstructure (local crystal structure and crystallite shapes). For example, FeB and Zn₄Si₂O₇Cl₂ have been reported recently with a structural study from X-rays only [8,9].

The in-situ study of the formation of MOFs under solvothermal conditions is largely unexplored. For example, one could study the transformation mechanism of the layered hydroxide MOF based on Mn²⁺ and thiophenedicarboxylate, Mn₂(OH)₂(C₆H₂O₄S), known to occur under hydrothermal conditions at 150 Celsius, towards Mn₃(OH)₂(C₆H₂O₄S)₂ [10]. This type of experiment should be easily set up, while possibly providing a method highlight.

A complex sequence of structural phase transitions is known in [CH₃NH₃][Co(COOH)₃] (*Pnma* at room temperature, a,b,c ≈ 8.4,8.7,8.11 Å), with transitions to modulated and monoclinic structures respectively around 140 K and 90 K [11]. Below 16 K, an antiferromagnetic order possibly associated with ferroelectric properties sets in, where a subtle symmetry change is observed in synchrotron powder diffraction but remains unsolved.

5.4. Energy materials

Electrode materials at different states of charge and discharge: powder recovered from electrochemical cells that have been cycled. The recovered powder is usually air sensitive so either loading at ESS if an argon glove box is available, or sample holders sent to the users that load and seal them in a glove box. The high-resolution and high-flux neutron diffraction studies could enable the accurate crystallographic determination of structural changes on cycling, such as cationic migrations, subtle transitions, and defects (antisite defects, stacking faults..), structural modifications (cation migration, phase segregation..) on aging (ex-situ samples) and Li localization. Examples include Layered Li-based and Na-based Ni-Mn-Co oxide compounds, and intergrowth structures [6], as well as NMC-type compounds that can benefit from contrast provided by neutrons between Ni, Mn, and Co.

The neutron diffraction studies of the solid electrolyte: Rb/Cs H₂PO₄, HKUST-1 Cu₃(benzene 1,3,5-tricarboxylate)₂(H₂O)₃ and argyrodite-type compounds [7] can be used to evaluate Li diffusion paths from measurements either at room temperature only or as a function of temperature to be able to refine anisotropic atomic displacement parameters and generate bond valence energy landscapes maps from the refined structures to correlate structure with ionic conductivity.

5.5. Incommensurate magnets

The possibility to capture, in a single experiment, Bragg signals that are typically measured separately on diffraction and SANS instruments, has high potential to help our understanding of a large class of materials that develop incommensurate magnetic orders.

The latter lead to satellites related to the chemical cell, including so-called 'zeroth satellites' around $Q=0,0,0$ that are often not possible to resolve on a diffractometer. Yet their observation together and scaled with the diffraction signals at higher momentum transfers is essential to the interpretation in terms of complex magnetic structures in quantum or functional materials, such as skyrmions. Examples skyrmion materials that would benefit from such measurements include (Tb,Y)Mn₆Sn₆, some CoZnMn chiral magnets, CeAlGe or MnGe. Access to both zero and higher-order satellites could help distinguish the contribution of itinerant electron magnetization.

6. REFERENCES

- [1] <https://indico.ess.eu/event/3387/>
- [2] G. Perversi et al. Nature Comm., 10, 2857 (2019)
- [3] E. Solana-Madruga et al. Angew. Chem., 61 9497 (2022)
- [4] K. Ji et al, ZAAC, 2023
- [5] J. Am. Chem. Soc. 2023, 145, 23, 12823–12836
- [6] Journal of The Electrochemical Society, 170(8) 2023
- [7] Nano Energy, Volume 83, May 2021, 105858
- [8] Acta Crystallographica Section A: Foundations of Crystallography 78, a147-a148
- [9] Angewandte Chemie 135 (26), e202303487
- [10] Inorganic Chemistry 52, 608-616 (2013)
- [11] IUCrJ 6, 105-115 (2019)

7. DOCUMENT REVISION HISTORY

Revision	Reason for and description of change	Author	Date
1	First issue	Florence Porcher	2024-10-02