Engineering and Physical Sciences Research Council

National Research Facility Annual Report Template

This annual report will be reviewed by the EPSRC National Research Facility High Level Group (HLG) with any feedback provided by EPSRC. The report and any feedback should be made available to your advisory committee and will also be used within EPSRC by your individual EPSRC contact and the EPSRC NRF lead for information and discussion.

Timeline 2023/24:

- Reporting Period for this Annual Report: **1st September 2022 – 31st August 2023**
- Deadline for Annual Reports**: 15th January 2024**
- Assessment by the HLG**: March 2024**
- Feedback to Facilities: **We aim to share feedback on your annual report in April 2024**

Please complete and return the Annual Report to (and cc: and) by 15th January 2024.

Information from a previous report can be included in this report **only** if it is marked with ** in the guidance below **and** the information is still applicable.

NRF ANNUAL REPORT

Facility Name:	**The UK High-Field Solid-State NMR Facility**
Director:	**Professor Steven P. Brown (University of Warwick)**
Start/End Dates	**5th January 2020 to 4th January 2025**
Funds awarded	**£2.4M (EP/T015063/1, to lead institution; related grants of total value £170k to Facility Executive PIs at other Universities: EP/T014121/1, EP/T01492X/1, EP/T014997/1, EP/T014911/1, EP/T014350/1)**

1) Value Proposition (max ½ page):

*Provide a brief description of how your facility is uniquely placed to provide for UK research** and a summary vision of how the capability aims to evolve.*

The UK High-Field Solid-State NMR National Research Facility (NRF) provides high-end provision for the solid-state NMR community in the UK that ensures its competitive edge internationally. The NRF serves a wide range of academic and industrial users across the disciplines from physical to life sciences enabling detailed molecular level characterisation of structures and dynamics of systems ranging from pharmaceuticals and catalysts to biomolecules, plants and advanced materials. The majority of users are expert solid-state NMR spectroscopists but, thanks to the guidance of highly experienced research technical professionals in the facility management team (FMT), the NRF increasingly accommodates non-expert users who are novices to solid-state NMR spectroscopy.

The NRF currently hosts the two highest field solid-state NMR spectrometers in the UK operating at 850 MHz and 1 GHz, which maximise resolution and sensitivity of the experiments. The spectrometers are equipped with an array of state-of-the-art rf probes that allow measurements for most nuclei across the periodic table under conditions ranging from very low to very high temperatures and static to ultrafast spinning. This rf probe technology is key to gaining maximum benefit from the high magnetic field. In this context, the Facility Executive (FE) through its carefully planned investment has ensured that the instrumentation remains cutting edge.

The value proposition is maximised by employing highly trained, expert personnel at a 'centre of excellence'. The facility managers, who are active scientists, both ensure retention of know-how about the cutting-edge methodology and are capable of quickly implementing new techniques and thus able to advise both expert and novice users on how to get most out of their experiments and optimise use of the available resources.

From 2025, the NRF will be expanded through addition of a 1.2 GHz NMR spectrometer that will run in a hybrid solid- and solution-state mode. We aim to expand the core expertise for the FMT by employing a technical professional with experience in biomolecular solution NMR spectroscopy. To maximise the return on the UKRI investment into ultrahigh field NMR and establish the most effective ways to serve the UK NMR community, we are working closely with the 1.2 GHz site at Birmingham and other 1.2 GHz sites around the world to optimise access mechanisms and adopt best practices.

2) Scientific Excellence and Scientific Impact

For the reporting period, please provide examples of how the facility supports scientific excellence in the UK. This should be a short narrative, including information on:

- *The breadth of research areas that are supported.** Highlight any new research areas.*
- *Important scientific breakthroughs that have been supported by the facility;*
- *New methodologies that have been developed;*

The High-field Solid-State NMR NRF supports cutting edge research across the chemical, materials and biological sciences by providing access to the highest magnetic field strengths available in the UK for solid-state NMR spectroscopy, as well as a range of specialist ancillary equipment. In 2023, the NRF delivered 20 publications in top journals including *Nature*, *Nature Plants*, the *Journal of the American Chemical Society*, *Angewandte Chemie* and *Advanced Materials*. A diverse range of research areas have been supported over the reporting period, including (but not limited to) fundamental chemistry, materials science, pharmaceutical science, plant biology and NMR methodology. We highlight below a few representative examples of the research carried out at the NRF and the impacts of this work.

One key area of research at the NRF is porous framework materials that have potential applications including catalysis and gas separation and storage. Ashbrook & co-workers used high-field ^{17}O NMR to study silicate zeolite frameworks prepared by the assembly-disassembly-organisation-reassembly (ADOR) process (*Cryst. Growth Des.*, 2023, 12, 8991). ADOR is a new approach that enables the preparation of novel zeolite topologies. However, many questions remain about the ADOR mechanism and, in particular, the chemical reactivity of Si-O-Si and Si-OH bonds and the roles this plays in the process. ^{17}O magic angle spinning (MAS) and multiple-quantum (MQ) MAS measurements at 20.0 and 23.5 T were used to gain insight into the ADOR mechanism and it was shown that oxygens within Si-O-Si bonds are exchangeable with H_2O under ambient conditions. This phenomenon is not observable by standard powder X-ray diffraction (PXRD) characterisation, which shows unchanged powder patterns in the early stages of the ADOR reaction. Furthermore, the high field was critical to enable resolution of distinct ^{17}O environments. This work has wider impact for the understanding of zeolite structures which have traditionally been thought to be chemically robust and inert, and yet have been revealed here by high-field NMR to be highly labile. Metal-organic frameworks (MOFs) are another important and widely studied class of porous materials. Schroder & co-workers used high-field ^{35}Cl

and ^{14}N NMR to probe the reactivity of NO_2 in a novel cationic MOF containing Cl^- counter ions within the pores (*Angew. Chem.*, 2023, 62, e202302602). ^{35}Cl and ^{14}N have low gyromagnetic ratios and large quadrupolar interactions; however, they provide the most direct insight into the reaction process in this system. At 23.5 T, it was possible to obtain a 2D ^{35}Cl-^{1}H dipolar correlation spectrum which revealed the location of Cl^- ions in the pores. ^{14}N-^{1}H dipolar correlations for pristine and NO_2-loaded MOFs showed pronounced changes at the methylpyridinium site, highlighting this as the reaction centre for the adsorbed NO_2. Ashbrook and co-workers used high-field ^{17}O NMR to study Al/Ga cation exchange in the well-known MOF MIL-53 (*Phys. Chem. Chem. Phys.*, 2023, 25, 20267). In mixed cation systems, distinct ^{17}O lineshapes are expected for bridging OH groups between Al/Al, Al/Ga and Ga/Ga arrangements, but the large ^{17}O quadrupolar interaction for each of these makes it difficult to separate them. By comparing experimental lineshapes recorded at 23.5 T with simulations for the different local OH environments, it was possible to deconvolute the experimental data and quantify the populations of each environment. It is important to note that this information on cation disorder is not possible to obtain from standard PXRD, which only provides information on the long-range, average structure. Furthermore, a common factor linking the two MOF studies cited is that they both target extremely challenging nuclei which would be difficult or unfeasible to study at lower field. The instrumentation at the NRF not only enabled observation and resolution of distinct environments, but also the implementation of more advanced 2D ^{35}Cl-^{1}H, ^{14}N-^{1}H and ^{17}O-^{1}H dipolar correlation experiments which provided precise structural constraints.

Another important group of inorganic materials is ion conductors which are of importance in the fields of battery and fuel cell research. Pasta & co-workers used high-field ^{23}Na NMR to study cation dynamics in Na_3OBr, which is of significant interest as a solid electrolyte in sodium metal batteries and displays unusual non-Arrhenius ionic conductivity (*Angew. Chem.*, 2023, 62, e202314444). Although ^{23}Na is a very sensitive nucleus, the large quadrupolar interaction in this structure (C_Q = 11.9 MHz) makes it challenging to observe at low field. Comparison of static spectra recorded at 20.0 T and 23.5 T enabled the quadrupolar parameters of ^{23}Na for Na_3OBr to be accurately determined, and also revealed the existence of significant weakly crystalline NaOH and Na_2O_2 impurities despite the fact that these were not observed in diffraction data. These impurities were found to play an important role in the non-Arrhenius ionic conductivity. Blanc & co-workers have exploited high-field and high-temperature NMR to study oxygen dynamics in the $La_{1+x}Sr_{1-x}Ga_3O_{7+0.5x}$ system which constitutes a promising family of fast oxide ion conductors (*J. Am. Chem. Soc.*, 2023, 145, 21817). Focusing on the composition $La_{1.54}Sr_{0.46}Ga_3O_{7.27}$, variable-temperature ^{17}O and ^{71}Ga MAS NMR measurements were recorded between 20 – 700 °C at 20.0 T. High-temperature measurements are necessary for this and similar systems because oxygen conduction typically takes place above 300 °C. Importantly, this work would not have been possible without the unique combination of the high magnetic field to resolve distinct environments *and* the expanded temperature range offered by the specialist laser probe available at the NRF.

The NRF has supported new research into organic systems, in particular pharmaceuticals. Brown & co-workers, in collaboration with Pfizer, used high-field solid-state NMR combined with DFT calculations to probe structure and disorder in active pharmaceutical ingredients (APIs). For Lorlatinib, an API used in the treatment of lung cancer, fast MAS and multidimensional ^{1}H-^{13}C, ^{14}N-^{1}H and ^{1}H-^{1}H dipolar correlation experiments at 23.5 T were used to probe the crystal structure and identify hydrogen-bonding interactions responsible for driving the crystal packing (*J. Pharm. Sci.*, 2023, 112, 1915). The resolution at 23.5 T was compared to that at 11.7 and 14.1 T, and it was shown that the high-field data enabled significantly more interatomic proximities to be identified in each type of experiment. In a separate study in collaboration with AstraZeneca, ^{35}Cl static NMR measurements at 23.5 T were used to examine structural disorder in a set of pharmaceutical hydrochloride salts (*ChemPhysChem*, 2023, 24, e202200558). Here, the high field was crucial to minimise the second-order quadrupolar broadening and maximise sensitivity. Combining this with high-field ^{1}H and ^{13}C NMR data revealed that trifluoperazine dihydrochloride exhibits a unique case of disorder involving the N^{+}–H hydrogen positions of the piperazinium ring which is difficult to characterise by diffraction.

The NRF supported a study of genetically engineered biomass which offers a potential alternative to non-renewable fossil-based resources for materials and energy (*Nature Plants*, 2023, 9, 1530). Poplar wood was engineered with the novel introduction of callose which resulted in increased enzymatic conversion to sugars and bioethanol. ^{13}C cross polarisation (CP) (MAS) and 2D spin-diffusion experiments at 20 T revealed that callose does not interact with other polymers but acts as a cell wall spacer, attracting water and making it much easier for enzymes to access/breakdown the wood. In the wider context, this important insight provides a new strategy for efficient biomass engineering towards useful products. ^{13}C NMR studies of enriched plant samples are challenging to study owing to low sensitivity (despite isotopic enrichment) and highly crowded spectra due to structural complexity. The high-field spectrometer used at the NRF enabled well-resolved spectra to be obtained in a feasible experimental time.

The NRF has also supported the development and understanding of NMR methodologies. Williamson & co-workers developed a new ^{19}F MAS NMR method to study membrane permeability of lipid vesicles towards model fluorinated drug molecules (*Angew. Chem.*, 2023, 62, e202301077). It was shown that ^{19}F MAS NMR at 20 T can be used to accurately determine the molar partition coefficient for a fluorinated drug into membranes of arbitrary complexity, providing the opportunity to study how cell membrane composition influences drug uptake. An important requirement of this approach is the ability to resolve drug populations in water and membrane phases, which are often separated by only a small chemical shift difference. The high magnetic field is therefore crucial to maximise the absolute frequency difference in order to accurately quantify the two populations. Lewandowski & co-workers used variable-temperature measurements at 20 and 23.5 T to quantify spin diffusion in a model dipeptide (*J. Chem. Phys.*, 2023, 158, 184201). Spin diffusion is widely used for magnetisation transfer in advanced correlation experiments, but the mechanics of the spin diffusion process depend on a complex range of factors relating to the sample and experimental conditions. The high-field and fast MAS / variable-temperature equipment at the NRF enabled a detailed study of the effect of the magnetic field and temperature on the spin diffusion process, while simultaneously maximising the resolution so that accurate data could be obtained for comparison with numerical simulations.

The above highlights do not represent an exhaustive account of the scientific excellence supported by the NRF during the reporting period, but serve to demonstrate how the world-class facilities are underpinning fundamental and applied research across a diverse range of fields and advancing the understanding of the technique itself. In the broader context, the cited examples show how the NRF is supporting emerging R&D trends and needs. For example, the increasing number of studies on materials for energy conversion and storage (as also exemplified in the new NRF Case Studies on Optoelectronic Materials, see #4) reflects the growing research interest as part of the wider move towards sustainable technologies in the R&D community. The NRF is playing a key role in supporting the development of these advanced materials and in many cases provides detailed structural information that is not possible to obtain by other methods. The collaborative studies with pharmaceutical companies highlight how the NRF is supporting industrially relevant research with leading commercial R&D organisations. The unique infrastructure within the NRF provides a level of structural insight into important and emerging APIs and therapeutics that is not possible with in-house academic or industrial characterisation facilities. Furthermore, the new NMR methodologies and fundamental insights into existing methodologies being provided by work at the NRF will have wider impacts in high-field NMR research as ≥ 1 GHz infrastructure becomes more accessible nationally and internationally.

3) Publications

*Please list the publications for the last 3 years of operation of the current award (by year) and identify any publications that have been prepared for a wider audience.***

From your list, please select 3 publications from the past year, provide a short paragraph to describe the research and how the facility has contributed to the publication. (You are encouraged to select 3 publications that showcase the diversity of research areas that the facility has supported or different ways the facility has contributed to research.)

*Provide a brief description of how you track publications and encourage users to inform you.***

It is a condition of use of the NRF that users acknowledge the NRF and specifically the EPSRC and BBSRC funding in publications and that users report these publications via an online form on the NRF website. In preparing the annual review, users are contacted to check that the publication information is correct and complete. Information of publications from previous use of the NRF by a specific PI is provided to the time allocation panel (TAP) when reviewing applications for time at the NRF. Users are also encouraged to produce snapshot videos (made available on the NRF YouTube channel, see #4 and #13) to make the key results from publications presenting NRF data more widely available. All publications are listed on the NRF website. In the below listing, we include a short summary to highlight the importance of each publication (key publications are featured in #2 above), also to illustrate the breadth of applications that are supported by the NRF (note also the wide range of journals where publications appear); the NRF asks the specific user to provide this summary.

The HLG feedback on our 2022 report stated "*The short summary on the contribution of the NRF in each publication was excellent and seen as best practice.*" We hence continue this for all publications below. The above scientific excellence and impact section (#2) provides a detailed commentary on 10 of these 2023 publications. The corresponding author(s) are indicated by * for the 2023 publications.

2023
Modulation of Uptake and Reactivity of Nitrogen Dioxide in Metal-Organic Framework Materials
Zi Wang, Alena M. Sheveleva, Daniel Lee, Yinlin Chen, Dinu Iuga, W. Trent Franks, Yujie Ma, Jiangnan Li, Lei Li, Yongqiang Cheng, Luke L. Daemen, Sarah J. Days, Anibal J. Ramirez-Cuesta, Bing Han, Alexander S. Eggeman, Eric J. L. McInnes, Floriana Tuna*, Sihai Yang*, Martin Schröder*
Angewandte Chemie International Edition 2023, 62 e202302602
DOI: 10.1002/anie.202302602
1 GHz spectrometer
A charged porous sorbent was designed to control the uptake and reactivity of corrosive air pollutants and conversion to a useful feedstock, namely a precursor for Nylon-6 synthesis. High-field solid-state NMR spectroscopy was required to detect the binding sites of the pollutants in the sorbent, allowing the reaction mechanism to be elucidated. This revealed a new type of "regenerable reactive adsorption" by modulating the charge in robust porous materials.

Investigations of the ADOR Process Using Solid-State NMR Spectroscopy
Cameron M. Rice, Olivia J. Dovernor, Russell E. Morris*, Sharon E. Ashbrook*
Crystal Growth and Design 2023, 12 8991–9000
DOI: 10.1021/acs.cgd.3c01037
1 GHz and 850 MHz spectrometers

^{29}Si and ^{17}O NMR spectroscopy is used to follow the assembly disassembly organization reassembly (ADOR) process for the transformation of a Ge-UTL zeolite. This demonstrates that the mechanism of the ADOR reaction is considerably more complex than initially proposed.

On the Origin of the Non-Arrhenius Na-ion Conductivity in Na_3OBr

Brigita Darminto, Gregory J. Rees, John Cattermull, Kenjiro Hashi, Maria Diaz-Lopez, Naoaki Kuwata, Stephen J. Turrell, Emily Milan, Yvonne Chart, Camilla Di Mino, Hyeon Jeong Lee, Andrew L. Goodwin, Mauro Pasta*

Angewandte Chemie 2023, 62 e202314444
DOI: 10.1002/anie.202314444

1 GHz and 850 MHz spectrometers

The sodium-rich antiperovskite Na_3OBr is a potential candidate as a solid electrolyte in next-generation sodium metal batteries. Non-Arrhenius ionic conductivities have been reported for this electrolyte the origin of which was not understood. This work applied temperature-resolved NMR methods to show that low-level impurities of Na_2O, Na_2O_2, and NaOH form a eutectic mixture at elevated temperatures causing this non-Arrhenius behaviour.

Carbon Vacancies Steer the Activity in Dual Ni Carbon Nitride Photocatalysis

Miriam Marchi, Edoardo Raciti, Sai Manoj Gali, Federica Piccirilli, Hendrik Vondracek, Arianna Actis, Enrico Salvadori, Cristian Rosso, Alejandro Criado, Carmine D'Agostino, Luke Forster, Daniel Lee, Alexandre C. Foucher, Rajeev Kumar Rai, David Beljonne, Eric A. Stach, Mario Chiesa, Roberto Lazzaroni, Giacomo Filippini*, Maurizio Prato, Michele Melchionna*, Paolo Fornasiero*

Advanced Science 2023, 10 2303781
DOI: 10.1002/advs.202303781

850 MHz spectrometer

The activity of a carbon nitride (CN) based photocatalyst was improved using a cost-effective microwave treatment. High-field solid-state ^{1}H fast-MAS NMR was employed to reveal the subtle structural changes resulting from this treatment. The high-resolution afforded by the high field and fast MAS enabled the detection of an increased amount of accessible NH moieties after microwave treatment that can readily bind Ni in these CN-Ni dual catalysts, which leads to enhanced activity.

Polymorphic Solid Solutions in Molecular Crystals: Tips, Tricks, and Switches

Adam Hill, Weronika Kras, Fragkoulis Theodosiou, Monika Wanat, Daniel Lee, and Aurora J. Cruz-Cabeza*

Journal of the American Chemical Society 2023, 145 20562-20577
DOI: 10.1021/jacs.3c07105

850 MHz spectrometer

Molecular crystalline organic solid solutions are very common, and are of large importance to the pharmaceutical industry. High-field solid-state ^{19}F NMR spectroscopy was used to evidence solid solution formation of 3-fluorobenzamide (guest) in benzamide (host). The high spectral resolution enabled the elucidation of conformational disorder of the fluorinated guest molecules, which depended on the final crystal structure of the solid solution. This highlighted a new strategy for organic crystal structure design.

Unraveling the Complex Solid-State Phase Transition Behavior of 1-Iodoadamantane, a Material for Which Ostensibly Identical Crystals Undergo Different Transformation Pathways

Okba Al Rahal, Benson M. Kariuki, Colan E. Hughes, P. Andrew Williams, Xiaoyan Xu, Simon Gaisford, Dinu Iuga, and Kenneth D. M. Harris*

Crystal Growth and Design 2023, 5 3820-3833
DOI: 10.1021/acs.cgd.3c00223

850 MHz spectrometer

Three low-temperature phases of 1-iodoadamantane (1-IA) were discovered, but remarkably, different crystals of the ambient-temperature phase (which are ostensibly identical at the level of information revealed by X-ray diffraction) were found to undergo different low-temperature phase transition pathways. Solid-state NMR data recorded at the NRF were crucial in establishing the dynamic properties of the 1-IA molecules in the ambient-temperature phase.

Ectopic callose deposition into woody biomass modulates the nano-architecture of macrofibrils
Matthieu Bourdon*, Jan J. Lyczakowski, Rosalie Cresswell, Sam Amsbury, Francisco Vilaplana, Marie-Joo Le Guen, Nadège Follain, Raymond Wightman, Chang Su, Fulgencio Alatorre-Cobos, Maximilian Ritter, Aleksandra Liszka, Oliver M. Terrett, Shri Ram Yadav, Anne Vatén, Kaisa Nieminen, Gugan Eswaran, Juan Alonso-Serra, Karin H. Müller, Dinu Iuga, Pal Csaba Miskolczi, Lothar Kalmbach, Sofia Otero, Ari Pekka Mähönen, Rishikesh Bhalerao, Vincent Bulone, Shawn D. Mansfield, Stefan Hill, Ingo Burgert, Johnny Beaugrand, Yoselin Benitez-Alfonso, Ray Dupree, Paul Dupree* and Ykä Helariutta*
Nature Plants 2023, 9 1530–1546
DOI: 10.1038/s41477-023-01459-0
850 MHz spectrometer
Callose (a polymer that is naturally occurring in some plant cell walls) was engineered into poplar wood and found that the wood is much more easily enzymatically converted into simple sugars and bioethanol than normal poplar. Solid-state NMR surprisingly revealed the reason for this is that callose does not interact with other polymers but acts as a cell wall spacer attracting water and making it much easier for enzymes to access/breakdown the wood.

Conformational Disorder in a Hybrid 2D Perovskite with a Long Aliphatic Chain under Pressure
Yulia Lekina, David G. Bradley, Yonghao Xiao, Adisak Thanetchaiyakup, Xin Zhao, Jagjit Kaur, Sudip Chakraborty, Han Sen Soo, John V. Hanna, and Ze Xiang Shen*
Journal of Physical Chemistry C 2023, 127, 16496–16507
DOI: 10.1021/acs.jpcc.3c02154
1 GHz spectrometer
^{1}H T_1 relaxation constants were measured for protons at different positions along a bulky hexadecylammonium (HDA) cation within a lead iodide perovskite lattice. The relaxation times were found to exhibit substantial variation, indicating that the aliphatic protons close to the NH_3^+ headgroup are more mobile and dynamic in comparison to the more rigid hydrophobic portion of the HDA chain.

Suppressed phase segregation for triple-junction perovskite solar cells
Zaiwei Wang, Lewei Zeng, Tong Zhu, Hao Chen, Bin Chen, Dominik J. Kubicki, Adam Balvanz, Chongwen Li, Aidan Maxwell, Esma Ugur, Roberto dos Reis, Matthew Cheng, Guang Yang, Biwas Subedi, Deying Luo, Juntao Hu, Junke Wang, Sam Teale, Suhas Mahesh, Sasa Wang, Shuangyan Hu, Eui Dae Jung, Mingyang Wei, So Min Park, Luke Grater, Erkan Aydin, Zhaoning Song, Nikolas J. Podraza, Zheng-Hong Lu, Jinsong Huang, Vinayak P. Dravid, Stefaan De Wolf, Yanfa Yan, Michael Grätzel, Merx G. Kanatzidis and Edward H. Sargent*
Nature 2023, 618, 74-78
DOI: 10.1038/s41586-023-06006-7
850 MHz spectrometer
This study used ^{133}Cs and ^{87}Rb at 20 T to determine the speciation of these two elements in new inorganic halide perovskite solar cell materials with improved stability under illumination. The high field was essential to provide spectral resolution, especially in the case of ^{87}Rb where it led to substantial narrowing of the central transitions relative to preliminary low field data.

Nuclear spin diffusion under fast magic-angle spinning in solid-state NMR
Ben P. Tatman, W. Trent Franks, Steven P. Brown and Józef R. Lewandowski

Engineering and Physical Sciences Research Council

Journal of Chemical Physics 2023, 158, 184201
DOI: 10.1063/5.0142201
1 GHz and 850 MHz spectrometers
Experimental results at 850 MHz and 1 GHz, including variable temperature ^{1}H MAS NMR spectra down to 175 K (using the Phoenix 1.9 mm probe), were recorded for a model dipeptide, to complement the theoretical and computer simulation of how spin diffusion occurs under fast MAS.

Leucopterin, the white pigment in butterfly wings: structural analysis by PDF fit, FIDEL fit, Rietveld refinement, solid-state NMR and DFT-D
Federica Bravetti, Lukas Tapmeyer, Kathrin Skorodumov, Edith Alig, Stefan Habermehl, Robert Huhn, Simone Bordignon, Angelo Gallo, Carlo Nervi, Michele R. Chierotti and Martin U. Schmidt*
IUCrJ 2023, 10, 448-463
DOI: 10.1107/S2052252523004281
1 GHz spectrometer
Leucopterin is a pigment found in the wings of butterflies. Its tautomeric forms in the solid state were unknown. This was investigated by high-field ^{1}H double-quantum MAS NMR spectroscopy combining it with lattice-energy minimizations using dispersion-corrected density functional theory (DFT-D) on 17 different possible tautomers. The density was found to be very high (1.909 kg dm^{-3}), and this helps to explain the good light-scattering and opacity.

Lipophilicity Modulations by Fluorination Correlate with Membrane Partitioning
Zhong Wang, Hannah R. Felstead, Robert I. Troup, Bruno Linclau*, Philip T. F. Williamson*
Angewandte Chemie International Edition 2023, 62, e202301077
DOI: 10.1002/anie.202301077
850 MHz spectrometer
The ability of a drug to cross the membrane to reach its site of action is determined by its lipophilicity. This paper describes how ^{19}F MAS NMR can be used to determine the molar partition coefficient for a fluorinated drug into membranes of arbitrary complexity. This provides the opportunity to study how membrane composition influences partitioning and permeability and their influence on drug uptake.

Disorder and Oxide Ion Diffusion Mechanism in $La_{1.54}Sr_{0.46}Ga_3O_{7.27}$ Melilite from Nuclear Magnetic Resonance
Lucia Corti, Dinu Iuga, John B. Claridge, Matthew J. Rosseinsky, and Frédéric Blanc*
Journal of the American Chemical Society 2023, 145, 21817-21831
DOI: 10.1021/jacs.3c04821
850 MHz spectrometer
^{17}O and ^{71}Ga MAS NMR spectroscopy, empowered by an ensemble-based computational approach to model site disorder, provides insight into the local structure in a family of oxide ion conductors with the melilite structure which is of high relevance owing to the excellent transport properties of its La-doped $La_{1.54}Sr_{0.46}Ga_3O_{7.27}$ phase. ^{17}O and ^{71}Ga high temperature MAS NMR experiments up to 700 °C acquired with the 7 mm laser-heated MAS probe available at the NRF provide evidence for the oxide ion conduction mechanism in $La_{1.54}Sr_{0.46}Ga_3O_{7.27}$.

Exploring cation distribution in ion-exchanged Al,Ga-containing metal–organic frameworks using ^{17}O NMR spectroscopy
Zachary H. Davis, Russell E. Morris* and Sharon E. Ashbrook *
Physical Chemistry Chemical Physics 2023, 25, 20267-20280
DOI: 10.1039/D3CP03071G
1 GHz and 850 MHz spectrometers
A mixed-metal metal-organic framework, (Al,Ga)-MIL-53, synthesised by post-synthetic ion exchange was investigated using ^{17}O NMR spectroscopy, providing site specific information on the metal

distribution. When the framework metal is exchanged using dissolved metal salts, NMR reveals the formation of crystallites with a core-shell structure, where the outer shell has a roughly equal ratio of Al^{3+} and Ga^{3+}. For metal exchange between two frameworks, no core-shell structure is observed, and instead crystallites containing a majority of Al^{3+} are obtained with lower levels of Ga^{3+}. In all cases, a slight preference for clustering of like cations is revealed using NMR.

Discovering the Solid-State Secrets of Lorlatinib by NMR Crystallography: To Hydrogen Bond or not to Hydrogen Bond
Zainab Rehman, W. Trent Franks, Bao Nguyen, Heather Frericks Schmidt, Garry Scrivens, Steven P. Brown*
Journal of Pharmaceutical Sciences 2023, 112, 1915-1928
DOI: 10.1016/j.xphs.2023.02.022
1 GHz spectrometer
Industry collaboration with Pfizer
Enhanced resolution at 1 GHz as compared to 600 MHz is demonstrated in two-dimensional ^{1}H-^{1}H double-quantum (DQ) and ^{1}H-^{13}C heteronuclear correlation (HETCOR) NMR spectra at 60 kHz MAS for the formulation solid-state form of Lorlatinib, a pharmaceutical for the treatment of lung cancer developed by Pfizer. Insight is provided into hydrogen bonding and CH-pi interactions that drive the adopted solid-state structure.

Toward Understanding of the Li-Ion Migration Pathways in the Lithium Aluminum Sulfides Li_3AlS_3 and $Li_{4.3}AlS_{3.3}Cl_{0.7}$ via $^{6,7}Li$ Solid-State Nuclear Magnetic Resonance Spectroscopy
Benjamin B. Duff, Stuart J. Elliott, Jacinthe Gamon, Luke M. Daniels, Matthew J. Rosseinsky, and Frédéric Blanc*
Chemistry of Materials 2023, 35, 27-40
DOI: 10.1021/acs.chemmater.2c02101
850 MHz spectrometer
Solid-state NMR was used to identify the Li-ion mobility mechanisms in two aluminium sulfide phases, Li_3AlS_3 and $Li_{4.3}AlS_{3.3}Cl_{0.7}$. The presence of immobile ions in Li_3AlS_3 was revealed from ^{7}Li line narrowing experiments and the release of these ions was facilitated through anion substitution of this phase to form $Li_{4.3}AlS_{3.3}Cl_{0.7}$. The absence of the immobile ions in $Li_{4.3}AlS_{3.3}Cl_{0.7}$ suggests an increased rate of ion exchange between the layers in this phase compared with Li_3AlS_3 as shown by high-field ^{6}Li-^{6}Li EXSY NMR along with ^{7}Li relaxometry.

Elucidating the Origins of High Preferential Crystal Orientation in Quasi-2D Perovskite Solar Cells
Lukas E. Lehner, Stepan Demchyshyn, Kilian Frank, Alexey Minenkov, Dominik J. Kubicki, He Sun, Bekele Hailegnaw, Christoph Putz, Felix Mayr, Munise Cobet, Günter Hesser, Wolfgang Schöfberger, Niyazi Serdar Sariciftci, Markus Clark Scharber, Bert Nickel, Martin Kaltenbrunner*
Advanced Materials 2023, 35, 2208061
DOI: 10.1002/adma.202208061
850 MHz spectrometer
This study determined the origin of highly preferential orientation in halide perovskite thin films prepared using one of the common fabrication strategies in the field employing a wide range of complementary techniques, including solid-state NMR. The high field proved useful to enable an exploratory study of ultrathin films of halide perovskites by maximising ^{13}C detection sensitivity.

Recent progress in solid-state NMR of spin-1/2 low-gamma nuclei applied to inorganic materials
Mark E. Smith*
Physical Chemistry Chemical Physics 2023, 25, 26-47
DOI: 10.1039/D2CP03663K

This review paper gives an account of recent progress made in the study of low-gamma nuclei in inorganic materials. High-field NMR offers particular advantages for the study of these challenging nuclei and in many cases enables observation that would not be possible at lower field. The review cites a number of studies carried out at the NRF.

Exploring the Potential of Multinuclear Solid-state ^{1}H, ^{13}C, and ^{35}Cl Magnetic Resonance To Characterize Static and Dynamic Disorder in Pharmaceutical Hydrochlorides
Patrick M. J. Szell, Zainab Rehman, Ben P. Tatman, Leslie P. Hughes*, Helen Blade, Steven P. Brown*
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Industry collaboration with AstraZeneca
1 GHz and 850 MHz spectrometers
Experimental wideline ^{35}Cl NMR spectra recorded at 20.0 and 23.5 Tesla, in combination with DFT calculations, are applied to three pharmaceutical HCl salts in an NMR crystallography study of the exhibited static and dynamic disorder.

2022

Al-Ani, A. J., Szell, P. M. J., Rehman, Z., Blade, H., Wheatcroft, H. P., Hughes, L. P.,* Brown, S. P.* & Wilson, C. C.* (2022). Combining X-Ray and NMR Crystallography to Explore the Crystallographic Disorder in Salbutamol Oxalate. *Crystal Growth and Design*, *22*, 4696–4707. DOI: 10.1021/acs.cgd.1c01093

Instrument: 850 MHz | *The enhanced resolution at high magnetic field in ^{1}H and ^{13}C spectra is invaluable in picking out low-intensity resonances due to the minor component for a C-OH centre that exhibits disorder. This collaboration with AstraZeneca demonstrates the value of combining complementary insight from solid-state NMR and X-ray diffraction.*

Berge, A. H., Pugh, S. M., Short, M. I. M., Kaur, C., Lu, Z., Lee, J.-H., Pickard, C. J., Sayari, A. & Forse, A. C.* (2022). Revealing Carbon Capture Chemistry with 17-Oxygen NMR Spectroscopy. *Nature Communications*, *13*, 7763. DOI: 10.1038/s41467-022-35254-w

Instruments: 850 MHz & 1 GHz | *First ^{17}O NMR experiments were carried out to study carbon dioxide capture mechanisms, which was only possible with the use of the high magnetic fields available at the NRF.*

Corsini, P. M., Wang, S., Rehman, S., Fenn, K., Sagar, A., Sirovica, S., Cleaver, L., Edwards-Gayle, C. J. C., Mastroianni, G., Dorgan, B., Sewell, L. M., Lynham, S., Iuga, D., Franks, W. T., Jarvis, J., Carpenter, G. H., Curtis, M. A., Bernadó, P., Darbari, V. C.* & Garnett, J. A.* (2022). Molecular and Cellular Insight into Escherichia Coli SslE and Its Role during Biofilm Maturation. *npj Biofilms and Microbiomes, 8*, 1–16. DOI: 10.1038/s41522-022-00272-5

Instrument: 850 MHz | *A new mechanism of biofilm formation in Escherichia coli is described: two-dimensional ^{35}Cl–^{1}H solid-state NMR spectra recorded at the NRF are presented to support fibrillation of the protein SslE.*

Fan, M., Xu, S., An, B., Sheveleva, A. M., Betts, A., Hurd, J., Zhu, Z., He, M., Iuga, D., Lin, L., Kang, X., Parlett, C. M. A., Tuna, F., McInnes, E. J. L., Keenan, L. L., Lee, D.*, Attfield, M. P.* & Yang, S.* (2022). Bimetallic Aluminum- and Niobium-Doped MCM-41 for Efficient Conversion of Biomass-Derived 2-Methyltetrahydrofuran to Pentadienes. *Angewandte Chemie International Edition*, *61*, e202212164. DOI: 10.1002/anie.202212164

Instrument: 850 MHz | *A heterogenous catalyst for highly-selective biomass conversion was developed based on a porous material atomically-doped with two metals, Al and Nb, and the NRF was used to prove that the Nb in this novel material was crucial to the efficient catalysis due to preferential adsorption of the biomass.*

Harris, K. D. M. (2022) NMR Crystallography as a Vital Tool in Assisting Crystal Structure Determination from Powder XRD Data. *Crystals*, *12*, 1277. DOI: 10.3390/cryst12091277

Instrument: 850 MHz | *This review of the significant role that NMR Crystallography can serve in facilitating and augmenting the process of crystal structure determination from powder XRD data included examples in which high-quality data recorded at the NRF in recent years played an important role in this field of research.*

Ke, Z., Dawson, D. M., Ashbrook, S. E.* & Bühl, M.* (2022) Origin of the Temperature Dependence of ^{13}C PNMR Shifts for Copper Paddlewheel MOFs. *Chemical Science*, *13,* 2674–2685. DOI: 10.1039/D1SC07138F

Instrument: 850 MHz | *This paper combining new computational methodology with challenging experiments, the 850 MHz spectrometer was used to confirm the field dependence, temperature dependence and dependence on MAS rate of the experimental measurements to evaluate the introduced theoretical approach.*

Luukkonen, T., Yliniemi, J.,* Walkley, B., Geddes, D., Griffith, B., Hanna, J. V., Provis, J. L., Kinnunen, P. & Illikainen, M. (2022) Characterization of an Aged Alkali-Activated Slag Roof Tile after 30 Years of Exposure to Northern Scandinavian Weather. *RSC Advances, 12*, 25822–25832. DOI: 10.1039/D2RA04456K

Instrument: 850 MHz | *The 30-year stability of roofing tiles and binder materials made using alkali-activated slag compositions were studied by ^{29}Si and ^{27}Al MAS NMR. The structural and chemical integrity of the original cast product was demonstrated to be intact at long-term freeze/thaw cycles under Scandinavian conditions.*

Luo, T., Wang, Z., Han, X., Chen, Y., Iuga, D., Lee, D., An, B., Xu, S., Kang, X., Tuna, F., McInnes, E. J. L., Hughes, L., Spencer, B. F., Schröder, M.* & Yang, S.* (2022) Efficient Photocatalytic Reduction of CO_2 Catalyzed by the Metal–Organic Framework MFM-300(Ga). *CCS Chemistry*, *4*, 2560–2569. DOI: 10.31635/ccschem.022.202201931

Instrument: 850 MHz | *Results recorded at the NRF were part of a variety of advanced analysis tools that were utilised to characterise a metal-organic framework (MOF) used for photocatalytic reduction of CO_2 and showed that the local environment of the metal (Ga) was highly-ordered, with this related to the exceptional stability of this material.*

Rusanova-Naydenova, D.,* Trublet, M., Klysubun, W., Cholsuk, C., Iuga, D., Dupree, R., Antzutkin, O. N. & Persson, I.* (2022) Synthesis and Structural Characterisation of Solid Titanium(IV) Phosphate Materials by Means of X-Ray Absorption and NMR Spectroscopy. *Dalton Transactions*, *51* , 8192–8207. DOI: 10.1039/D2DT00902A

Instrument: 850 MHz | *$^{47/49}Ti$ and ^{31}P-^{31}P NOESY NMR experiments were used to characterise linked titanium phosphate compounds, which are promising materials for wastewater treatment for removal of metal ions and complexes.*

Smalley, C. J. H., Hoskyns, H. E., Hughes, C. E., Johnstone, D. N., Willhammar, T., Young, M. T., Pickard, C. J., Logsdail, A. J., Midgley, P. A. & Harris, K. D. M. *(2022) A Structure Determination Protocol Based on Combined Analysis of 3D-ED Data, Powder XRD Data, Solid-State NMR Data and DFT-D Calculations Reveals the Structure of a New Polymorph of L-Tyrosine. *Chemical Science*, *13*, 5277–5288. DOI: 10.1039/D1SC06467C

Instrument: 850 MHz | *A structure determination protocol based on combined analysis of 3D-ED data, powder XRD data, solid-state NMR data and DFT-D calculations reveals the structure of a new polymorph of L-tyrosine.*

Smalley, C. J. H., Logsdail, A. J., Hughes, C. E., Iuga, D., Young, M. T. & Harris, K. D. M.* (2022) Solid-State Structural Properties of Alloxazine Determined from Powder XRD Data in Conjunction with DFT-

D Calculations and Solid-State NMR Spectroscopy: Unraveling the Tautomeric Identity and Pathways for Tautomeric Interconversion. *Crystal Growth & Design, 22*, 524–534. DOI: 10.1021/acs.cgd.1c01114

Instrument: 850 MHz | *While different tautomeric structures of alloxazine give a comparable quality of fit to powder XRD data as they differ only in the positions of a subset of the hydrogen atoms in the molecule, the tautomeric form present in the crystal structure could be definitively identified based on high-resolution solid-state ^{15}N NMR data recorded at the NRF.*

Tognetti, T., Franks, W. T., Lewandowski, J. R. & Brown S. P.* (2022) Optimisation of ^{1}H PMLG homonuclear decoupling at 60 kHz MAS to enable ^{15}N–^{1}H through-bond heteronuclear correlation solid-state NMR spectroscopy. *Physical Chemistry Chemical Physics*, *24*, 20258–20273 DOI: 10.1039/d2cp01041k

Instrument: 1 GHz |*Improved methods for homonuclear decoupling at fast MAS are developed in the high and low power regime. The improvements in ^{1}H resolution thanks to the combination of this methodology and high field are demonstrated, noting that this represents the first example of a new paradigm in homonuclear ^{1}H decoupling, namely where the ^{1}H nutation frequency is less than the MAS frequency.*

Whewell, T., Seymour, V. R., Griffiths, K., Halcovitch, N. R., Desai, A. V., Morris, R. E., Armstrong, A. R. & Griffin, J. M.* (2022) A structural investigation of organic battery anode materials by NMR crystallography. *Magnetic Resonance in Chemistry, 60*, 489–503 DOI: 10.1002/mrc.5249

Instrument: 1 GHz | *In a materials characterisation paper, a two-dimensional ^{23}Na MQMAS NMR spectrum recorded at 23.5 T is shown for a new phase of sodium naphthalenedicarboxylate which shows that five distinct sodium environments are present in the structure – something which could not be unambiguously determined in lower magnetic field NMR experiments.*

Yu, L., Yoshimi, Y., Cresswell, R., Wightman, R., Lyczakowski, J. J., Wilson, L. F. L., Ishida, K., Stott, K., Yu, X., Charalambous, S., Wurman-Rodrich, J., Dupree, R., Terrett, O. M., Brown, S. P., Temple, H., Krogh, K. B. R. M. & Dupree, P.* (2022). Eudicot primary cell wall glucomannan is related in synthesis, structure and function to xyloglucan. *The Plant Cell*, *34*, 4600-4622 DOI: 10.1093/plcell/koac238

Instrument: 850 MHz & 1 GHz | *The exquisite resolution provided at high field in 2D refocused INADEQUATE ^{13}C MAS NMR spectra allows resonances for the separate biopolymers to be picked out, uniquely yielding insight into differences in mobility.*

Vashishtha, P.,* Griffith, B. E., Fang, Y., Jaiswal, A., Nutan, G. V. Bartók, A. P. White, T. J. & Hanna, J. V.* (2022). Elucidation of the Structural and Optical Properties of Metal Cation (Na^+, K^+, and Bi^{3+}) Incorporated $Cs_2AgInCl_6$ Double Perovskite Nanocrystals. *Journal of Materials Chemistry*, *A10*, 3562-3578 DOI: 10.1039/d1ta08263a

Instrument: 850 MHz | *Multinuclear MAS NMR and calculations have demonstrated that the improved optical properties from Na^+, K^+, Bi^{3+} cation substituted $Cs_2AgInCl_6$ double perovskite nanocrystal systems are attributed to increased covalency and structural rigidity, with optimal performance demonstrated by K^+ incorporation which exhibits an affinity for A and B site substitution.*

2021

Al Rahal, O., Williams, P. A., Hughes, C. E., Kariuki, B. M., & Harris, K. D. M.* (2021). Structure determination of multicomponent crystalline phases of (S)-ibuprofen and l-proline from powder X-ray diffraction data, augmented by complementary experimental and computational techniques. *Crystal Growth & Design*, *21*, 2498–2507 DOI: 10.1021/acs.cgd.1c00160

Two multicomponent crystalline phases of (S)-ibuprofen and L-proline are reported, with structure determination carried out directly from powder XRD data, augmented by information from high-field solid-state NMR, thermal analysis and periodic DFT-D calculations.

Engineering and Physical Sciences Research Council

Chen, C. H.,* Mentink-Vigier, F., Trebosc, J., Goldberga, I., Gaveau, P., Thomassot, E., Iuga, D., Smith, M. E., Chen, K. Z., Gan, Z. H., Fabregue, N., Metro, T. X., Alonso B.,* & Laurencin D*. (2021). Labeling and Probing the Silica Surface Using Mechanochemistry and ^{17}O NMR Spectroscopy. *Chemistry – A European Journal. 27*, 12574–12588 DOI: 10.1002/chem.202101421

Novel mechanochemical approaches to oxygen-17 enrichment were extended mixed SiO_2-TiO_2 systems. A comprehensive NMR methodology was employed which included exploiting the magnetic field variation of the spectra, as well as spatially dependent measurements to elucidate the labelling mechanism.

Cross, C., Cervini, L., Halcovitch, N. R., & Griffin, J. M.* (2021). Solid-state nuclear magnetic resonance study of polymorphism in tris(8-hydroxyquinolinate)aluminium. *Magnetic Resonance in Chemistry 59*, 1024–1037 DOI:10.1002/mrc.5147

An aluminium coordination complex of interest for organic light-emitting diode technology is investigated by solid-state NMR and DFT calculations. This work resolves a long-standing debate about the polymorphic structures of this material which are subtly different and difficult to distinguish by diffraction. It also allows one proposed structure to be ruled out on energetic considerations.

Dawson, D. M.,* Macfarlane, L. E., Amri, M., Walton, R. I., & Ashbrook, S. E.* (2021). The Thermal Dehydrofluorination of GaPO-34 Revealed by NMR Crystallography. *Journal. of Physical Chemistry C. 125*, 2537-2545 DOI:10.1021/acs.jpcc.0c1087

High-field Ga NMR experiments were key in characterising an unusual phase transition in a gallophosphate framework, showing the new material is stabilised by the binding of the structure directing agent to give a five-coordinate Ga centre and a purely neutral, but templated, framework.

de Andrade, P., Muñoz-García, J. C., Pergolizzi, G., Gabrielli, V., Nepogodiev, S. A., Iuga, D., Fábián, L., Nigmatullin, R., Johns, M. A., Harniman, R., Eichhorn, S. J., Angulo, J., Khimyak, Y. Z.,* & Field, R. A.* (2021). Chemoenzymatic synthesis of fluorinated cellodextrins identifies a new allomorph for cellulose-like materials. *Chemistry – A European Journal*, *27*, 1374-1382. https://doi.org/10.1002/chem.202003604

Fluorinated constituents are incorporated into self-assembled crystalline materials where a new allomorph is formed as characterized by ^{19}F, ^{1}H, and ^{13}C NMR experiments performed at the NRF.

Gamon, J., Dyer, M. S., Duff, B. B., Vasylenko, A., Daniels, L. M. Zanella, M., Gaultois, M. W. Blanc, F., Claridge, J. B., and Rosseinsky M. J.* (2021). $Li_{4.3}AlS_{3.3}Cl_{0.7}$: A Sulfide-Chloride Lithium Ion Conductor with Highly Disordered Structure and Increased Conductivity. *Chemistry of Materials. 33*, 8733–8744 DOI: 10.1021/acs.chemmater.1c02751

The coordination environment of the Al sites in the computationally discovered and experimentally realised Cl-doped Li_3AlS_3 fast Li^+ ion conductor was solved using the enhanced resolution of the ^{27}Al NMR spectrum achieved at the high field facility.

Gardner, L. J., Walling, S. A. Lawson, S. M. Sun, S., Bernal, S. A., Corkhill, C. L., Provis, J. L., Apperley, D. C., Iuga, D., Hanna, J. V., & Hyatt, N. C.* (2021). Characterization of and Structural Insight into Struvite-K, $MgKPO_4.6H_2O$, an Analogue of Struvite. *Inorganic Chemistry, 60*, 195-205 DOI: 10.1021/acs.inorgchem.0c02802

The NRF enabled recording of ^{25}Mg and ^{39}K solid-state NMR spectra of Struvite-K, a magnesium potassium phosphate mineral with naturally cementitious properties, which is finding increasing usage as an inorganic cement for niche applications including nuclear waste management and rapid road repair.

Hughes, A. R., Liu M., Paul S., Cooper A. I., & Blanc, F.* (2021). Dynamics in Flexible Pillar[n]arenes Probed by Solid-State NMR. *Journal of Physical Chemistry C, 125*, 13370-13381 DOI: 10.1021/acs.jpcc.1c02046

Very high field ^{1}H NMR combined with very fast magic angle spinning and two-dimensional experiments revealed inter- and intra-molecular interactions in host-guest interactions in a new class of supramolecular assemblies. Only the resolution achieved at very high field (here 850 MHz) enables those interactions to be revealed.

Iuga, D.,* Corlett, E. K. & Brown, S. P. (2021). ^{35}Cl-^{1}H Heteronuclear correlation magic-angle spinning nuclear magnetic resonance experiments for probing pharmaceutical salts. *Magnetic Resonance in Chemistry 59*, 1089-1100 DOI: https://doi.org/10.1002/mrc.5188

In a method development paper, two-dimensional ^{35}Cl–^{1}H solid-state NMR spectra recorded at the NRF are presented for a range of HCl salts, including for the pharmaceuticals cimetidine, amitriptyline and lidocaine.

Jones, C. L., Hughes, C. E., Yeung, H. H.-M., Paul, A., Harris, K. D. M.* & Easun, T. L.* (2021). Exploiting in-situ NMR to monitor the formation of a metal-organic framework. *Chemical Science*, *12*, 1486–1494 DOI: 10.1039/D0SC04892E

Formation of the MOF material MFM-500(Ni) was probed using an in-situ NMR strategy that gives information on the time-evolution of the reaction and crystallization processes, yielding detailed insights on the solution-phase processes and kinetics of crystallization.

Laurencin, D.,* Li Y., Duer M. J.,* Iuga D., Gervais C., & Bonhomme, C.* (2021). A ^{43}Ca nuclear magnetic resonance perspective on octacalcium phosphate and its hybrid derivatives. *Magnetic Resonance in Chemistry 59,* 1048-1061 DOI: 10.1002/mrc.5149

The NRF enables recording ^{43}Ca experiments, including using double-resonance ^{43}Ca-^{1}H and ^{43}Ca-^{31}P techniques, for octacalcium phosphate and hybrid derivatives involving intercalated metabolic acids namely, citrate, succinate, formate, and adipate, so yielding insight into complex hybrid biomaterials.

Leroy, C., Bonhomme-Coury, L., Gervais, C., Tielens, F., Babonneau, F., Daudon, M., Bazin, D., Letavernier, E., Laurencin, D., Iuga, D. Hanna, J. V., Smith, M. E., & Bonhomme C.* (2021). A novel multinuclear solid-state NMR approach for the characterization of kidney stones. *Magnetic Resonance,* 2, 653–671 DOI: 10.5194/10.5194/mr-2-653-2021

Understanding the underlying chemical processes that determine the structures of pathological calcifications such as kidney stones underpins better treatments. A fully multinuclear NMR approach was employed including ^{1}H-^{1}H SQ-DQ BABA experiments and ^{43}Ca MAS NMR at the National Facility where subtle variations of the calcium siting could be observed.

Ma, Y., Han, X., Xu, S., Wang, Z., Li, W., da Silva, I., Chansai, S., Lee, D., Zou, Y., Nikiel, M., Manuel, P., Sheveleva, A. M., Tuna, F., McInnes, E. J. L., Cheng, Y., Rudić, S., Ramirez-Cuesta, A. J., Haigh, S. J., Hardacre, C., Schröder, M.,* & Yang, S.* (2021). Atomically Dispersed Copper Sites in a Metal−Organic Framework for Reduction of Nitrogen Dioxide. *Journal of the American Chemical Society*, *143*(29), 10977-10985. https://doi.org/10.1021/jacs.1c03036

The combination of high field and fast magic angle spinning available at the NRF enabled the nature of ^{1}H environments at defect sites of metal-organic framework UiO-66(Zr) to be determined. This helped locate the active sites responsible for efficient NO2 reduction in Cu/UiO-66(Zr).

Pawlak T.,* Sugden I., Bujacz, G., Iuga, D., Brown, S. P., & Potrzebowski, M. J. (2021). Synergy of Solid-State NMR, Single-Crystal X-ray Diffraction, and Crystal Structure Prediction Methods: A Case Study of

Teriflunomide (TFM). *Crystal Growth & Design*, *21*, 3328–3343 DOI: 10.1021/acs.cgd.1c00123

Low-temperature ^{13}C spectra recorded at the NRF allow the phase transition between two polymorphs of the pharmaceutical, teriflunomide, that has been approved for multiple sclerosis treatment to be observed directly.

Pugliese, A., Toresco, M., McNamara, D., Iuga, D. Abraham, A., Tobyn, M. Hawarden, L. E., and Blanc F.* (2021). Drug–Polymer Interactions in Acetaminophen/Hydroxypropylmethylcellulose Acetyl Succinate Amorphous Solid Dispersions Revealed by Multidimensional Multinuclear Solid-State NMR Spectroscopy. *Molecular Pharmaceutics. 18*, 3519-3531 DOI: 10.1021/acs.molpharmaceut.1c00427

Well-resolved ^{1}H ^{14}N HMQC experiments at the high field facility recorded on several acetaminophen cellulose-derived amorphous solid dispersions were key to enable identification of spatial interactions that stabilisation these formulations.

Smith, M. E. (2021). Recent progress in solid-state nuclear magnetic resonance of half-integer spin low-gamma quadrupolar nuclei applied to inorganic materials. *Magnetic Resonance in Chemistry 59*, 864–907 DOI: 10.1002/mrc.5116

Solid-state NMR of half-integer quadrupolar nuclei with small magnetic moments and their application to understanding inorganic materials are discussed in this invited review. It is clearly shown that through access to NMR capability such as provided by the National Facility that the utility of such nuclei has greatly expanded.

4) Case studies (this section will be taken into account but not individually scored)

Please include up to 3 new case studies. One of which should focus on less traditional case study areas such as: working with other facilities/institutes, resolving a major issue, outreach. Please do not include a previously reported case study unless there has been significant progress since it was last reported.

Three new case studies (appended to the end of this report) are presented on:

1. Optoelectronic materials

2. Soft matter

3. Training Activities (in collaboration with Connect NMR UK)

We have uploaded these to our NRF website that also gives access to case studies from previous years. https://warwick.ac.uk/fac/sci/physics/research/condensedmatt/nmr/850/case_studies/

5) Training, Outreach and Non-Scientific Impacts

This section includes training, outreach, and societal, economic and environmental impacts. For the reporting period please provide information on the broader impact that the facility has through its outreach and training activities. This should include:

- *Brief description of training courses and workshops held by the facility for its users / potential users and any benefits highlighted by the participants;*
- *Brief description of facility staff training activities and other actions taken to support their career development;*
- *Activities to promote the facility beyond its core user base;*
- *Public engagement activities;*

- *Examples of any societal, economic and environmental impacts that the facility has created or been involved with.*

The NRF Annual Symposium in March/April is now a well-established event in the UK solid-state NMR community. Following on from the success of the 2022 Symposium, which was the first time that a hybrid format was used, a 44% increase in attendance was achieved in 2023. The 2023 Annual Symposium (in March) had 187 attendees, of which 75 were in person. The symposium featured an invited international speaker (Prof. Olivier Lafon) as well as seven NRF users from across the UK, of whom two were PhD students and one PDRA. The Technical Director, Dr Iuga, gave a talk entitled "*Solid State NMR probe design and build*". The attendees were from a mix of academic and industrial backgrounds (AstraZeneca, BASF, Bruker, JEOL and Pfizer), reflecting the broad areas of applications enabled by the NRF. Geographically, the event attracted attendees not only from the UK and Europe (Austria, Belgium, France, Germany, Italy, Poland, Slovakia, Slovenia) but also further afield including the US, Canada, Australia, India, UAE, South Korea, Saudi Arabia, and South Africa, illustrating the capability of the hybrid format and underlining the international reputation of the NRF.

The second Connect NMR UK workshop was held on the day preceding the Annual Symposium and delivered by FE and FMT members, again following the success of the 2022 event. The 15 participants (3 PhD students, 3 postdocs, 6 technical experts/research officers and 3 academics), all of whom are solution-state NMR spectroscopists with no or very little solid-state NMR experience, received a lecture focused on anisotropic interactions in the solid state (Prof. John Griffin, Lancaster). The group was then subdivided into hands-on workshops in the afternoon covering rotor packing (Dr Dinu Iuga and Dr Trent Franks) and experimental techniques including fast MAS, ^{13}C CP, and MQMAS (Prof. Frédéric Blanc, Liverpool, at the 1 GHz NMR spectrometer).

In this reporting period, over 50% of the NRF access for PhD students (35) and PDRAs (16) was by users who are new to the facility (see #7), proving that the NRF provides an invaluable platform for training the next generation of scientists on cutting-edge infrastructure. 6 of the PhD students and 2 of the PDRA users work on projects with industry support. Dr Stephen Day (Johnson Matthey) represents the interests of industrial users on the facility Oversight Committee (OC). In the framework of the preparations for 1.2 GHz NMR in the UK (see #13), a joint Warwick-Birmingham 1.2 GHz industry group has been set up (first meeting was in October 2023), bringing together scientists from AstraZeneca, Bristol Myers Squibb, C4X, GlaxoSmithKline, Johnson Matthey, Quotient Sciences, Sygnature Discovery and Syngenta.

Facility staff have carried out career development activities, often contributing to the profile of the NRF at the same time. Dr Dinu Iuga, the NRF Technical Director, has been active in grant applications: including applying for an EPSRC Impact Acceleration Account (IAA) grant in collaboration with Cryogenics Ltd. on building static and MAS probes, and was co-I on the "Network of Research Technical Professionals (RTPs) working in the UK's high field magnet facilities" grant proposal. He has successfully obtained spectrometer time at the US National High Magnetic Field Laboratory (NHMFL) in Florida to access specialist hardware for a collaborative project on ^{67}Zn NMR (visited in October 2023). In April and June 2023, Dr Trent Franks, the 1 GHz Facility Manager, participated in the University of Warwick Science Facility Roadshow held at two different locations on campus to publicise the NRF capabilities to potential collaborators and users. Dr Franks had a poster presentation on his own research at the EUROMAR meeting in Glasgow (June 2023). Other external presentations by the FMT are detailed in #12. Dr Iuga and Dr Franks are co-authors on 4 and 3, respectively, of the 2023 NRF publications (see #3).

The NRF continues to engage with the scientific and general community via its web presence and social media channels. The website receives over 1,000 visits per month, of which the majority are external and from at least 850 distinct devices (see #14). To enhance transparency of the decision-making process at the NRF, we have provided the facility annual report and feedback received from 2020 onwards on our website (with agreement of EPSRC). On X (formerly Twitter), the number of followers has increased from 454 to 598, with a peak of 7,000 tweet impressions in October 2022 associated with the announcement of the £17M UKRI award for the 1.2 GHz spectrometer (see #14).

6) Cost Recovery

*Please report on the sustainability returns for each year of operation of the current award.** Using the table below, please provide the running/operational costs for each year (£), the total amount incurred through grants (£), other academic users/sources (£), industrial users (£) and other income sources, and an overall % recovery (i.e., total income divided by the annual running cost).*

*Below the table, please state whether students pay to access your facility and if so, please provide further information on the number of student users for each year** and the % of students that have paid for access.*

*Also, provide a narrative of any future plans and issues identified related to cost recovery.***

Year	Running Costs	Grants	Other Academic	Industry	Other*	%
1/20 – 8/20	£154,013	£23,965		£2,000		17
9/20 – 8/21	£267,156	£22,925		£2,000		9
9/21 – 8/22	£342,995	£12,637		£6,000		5
9/22 – 8/23	£404,556	£21,257		£2,000	£37,885	15
Total	£1,168,720	£80,784		£12,000	£37,885	11

*EU PANACEA Transnational access funding (see below text)

NB: The NRF does not charge for PhD (or undergraduate project) student access.

The above table reports income (net, i.e., without VAT) that was credited during the reporting period NRF according to three cost recovery income mechanisms:

(i) "Grants": Funded days on grant applications

Prior to application, the PI fills out a webform describing the solid-state NMR experiments to be performed. This is reviewed by the Technical Director, Dr Dinu Iuga, who provides a technical assessment of the viability of the proposed high-field NMR experiments that is uploaded with the grant application. For UKRI applications, the procedure (in use since 2016) is to specify the total number of days ("Units") and the total access charge (£917 per day plus VAT where applicable, "Cost").

(ii) "Industry": Directly funded use by industry via contract for confidential research (current rate of £2,000 per day + VAT, with a discounted taster rate of £1,000 per day for first use by new companies)

(iii) "Other": PANACEA (to allow ready distinguishing from income on UKRI grants, we report this in the Other column). This corresponds to the first reporting period (18 months to end of February 2023), with £9,027 for cryogens and £28,858 for FMT and administrator salaries.

We report in the above Table, the NRF "Running Costs" are stated as direct costs, i.e., consumables and user travel and accommodation and direct salary costs of the FMT and the Administrator. The separate break down (for full years) is salary £171,373 (to 8/23), £177,364 (to 8/22), £152,784 (to 8/21), and other costs £233,183 (to 8/23), £165,631 (to 8/22), £114,372 (to 8/21).

Over the current 5-year NRF funding period that started in January 2020, the funding provided by EPSRC tapers down from 80% to 60% of total costs in a 5% step each year, i.e., the average is 70% over the 5 years. Compared to the baseline of 80% costs (i.e., that for a standard EPSRC grant), this corresponds to a target of 10% cost recovery each year. As such, helped by the PANACEA grant income, the NRF is achieving this target. However, moving forward, the FE is aware that a recovery of at least 20% needs to be reached, and with ever higher running costs (noting a substantial increase in the cost of cryogens), this has not been reached in the Sept 2022 to Aug 2023 period.

In Summer 2023, the Director commissioned the FE member, Prof. Mark Smith, to prepare a paper exploring how to achieve better financial sustainability through improved understanding of the underlying drivers of sustainability and how to incentivise more direct income generation. A preliminary discussion was held at the October 2023 FE meeting. A first trial change to the time allocation application process was agreed (and implemented for the October 31st 2023 round), whereby the PI is requested to explain why NRF grant funded days were not requested in a grant application if a PDRA is named among the visitors. The meeting also agreed on areas to be explored in a further paper at the next FE meeting (April 2024). This work has improved understanding of where the shortfall occurs and the most likely routes to be targeted for increased direct income generation. Work will also be carried out directly with other NRFs to better define what best practice is as well as to understand if a level playing field is operating across the whole NRF portfolio. The FE has agreed to undertake this work, although it would be more efficient if this was convened by EPSRC. Given the emphasis that EPSRC is placing on achieving financial sustainability, the work has also identified that more scrutiny needs to be placed on those applicants/organisations that are benefitting the Facility (see #7 below), i.e., could they be considered to effectively get a ‘free ride’ from EPSRC/BBSRC funding. The FE will think about how to attract funding from these sources.

7) Users

*Please report on the number of Users by year of operation of the current award.** This needs to be broken down by the category of user using the table below. We would like to know unique user numbers and repeat user figures. How many of the users are new as a % of users this year? If possible, please also record the number of unique user groups.*

*Indicate the research area split using a chart below the table and how this is measured** (e.g., samples/project types etc). A narrative of future plans and issues is required below the table.*

Note that the reported timeline here and in other below sections corresponds to the NRF’s 6-monthly time-allocation periods, i.e., the combined total for two cycles that most closely match the NRF reporting period is stated, namely July 2022 to June 2023, combined for the NRF’s two solid-state NMR spectrometers at 850 MHz and 1 GHz.

July 2022 to June 2023	PhD Student		PDRA		Academic (PI)		Industry		Other	
Total unique users	35[a]		16[b]		35[c]		1[d]		15[e]	
New users	20	57%	8	50%	11	31%	0	0%	10	67%

[a] Funded by EPSRC (8, including via the Green CDT in partnership with NNL, and 3 with additional industry support from GlaxoSmithKline and Johnson Matthey), Faraday Institution (3), BBSRC (1), The Leverhulme Trust (2), ERC (2), Chinese Government Scholarship (1), British Heart Foundation (1), industry funding (3, Bruker, Johnson Matthey, and Infineum), University funding, including 6 via external donations (4). 2 overseas PhD students of a collaborator (France) of a UK PI. Visitors via the EU funded PANACEA project (6, of which 5 are new).
[b] Funded by EPSRC (4, 1 of which is a Prosperity Partnership grant with Mitsubishi Chemicals), Faraday Institution (1), MRC (1), NERC (2), ERC (1, UK guarantee scheme administered by Innovate UK), US Department of Energy (1), industry (1, Infineum), charity (1, Howard Dalton for antimicrobial resistance research), University pump-priming (1). 3 new visitors via the EU funded PANACEA project.
[c] 27 applicants, of which 4 new, to the TAP process (see #11 KPI table for University and Department information); 3 new Fast-Track applicants; 5, of which 4 new, EU-funded PANACEA applicants.
[d] Johnson Matthey
[e] Including 6 (of which 2 are new) University research staff. Visitors via the EU funded PANACEA project (2, of which 1 is new). Three undergraduate students (all new). Four (all new) A-level students from local schools (Summer widening participation visitors).

The research split (by day of usage, for TAP awarded, fast-track, grant-funded including via the EU PANACEA project and industry days; categories determined by the FMT) is presented below:

Research area split	Materials		Bio-molecular solids (including plant cell walls)		Methods		Pharmaceuticals and self-assembly	
	days	%	days	%	days	%	days	%
July to Dec 2022 (850 MHz)	107	17%	15	2%	0	%	31	5%
July to Dec 2022 (1 GHz)	76	12%	63	10%	0	%	31	5%
Jan to June 2023 (850 MHz)	134	21%	12	2%	0	%	16	3%
Jan to June 2023 (1 GHz)	50	8%	89	14%	0	%	14	2%
Combined	367	58%	179	28%	0	%	92	14%

The above statistics reflect the importance of the NRF to a wide range of science applications (see also #2 and #3) across EPSRC and also the BBSRC, MRC and NERC remits. In addition, the significant number of PhD student users with industry support (6) is noted: while the number of directly paid for industry days is low (see #6 and #9), this shows the high relevance of the facility to industry sectors including pharmaceuticals and fine chemicals.

The NRF continues to place an emphasis on expanding the user base (see also #5). We draw attention to one mechanism by which new PIs who are not solid-state NMR experts are helped along the process of making an application for time to the 6-monthly TAP: namely test days provided by the FMT after an email inquiry. This is reported as a new KPI (#11), corresponding to inquiries to the FMT from potential new users. The OC is provided with a detailed commentary on each inquiry, the NRF response and whether experiments have been carried out at the NRF.

8) User Surveys/Satisfaction

*Please share a summary of any user surveys, including how many users asked and replied and how this has affected facility planning. Please include details of additional methods that the facility uses to collect user satisfaction data** and the results.*

Average scores (July 2022 – June 2023, the NRF's time allocation periods)
Rating : 1 Low / 5 High

PI feedback questionnaires (29 sent, 22 responses received: requested once per year)

Q1. The ease of the application process	4.9
Q2. The transparency of the allocation procedure	4.7
Q3. The feedback on time requests	4.7
Q4. The scheduling of your time by the facility	4.8
Q5. Quality of results obtained at the facility	4.5

Visitors feedback questionnaires (43 sent, 22 responses received) - Requested every six months after every time allocation round.

Q1. Ease of arranging accommodation	4.7
Q2. Quality of accommodation	4.7
Q3. Location of accommodation	4.9
Q4. Support from FM upon arrival	4.7
Q5. Support throughout your visit	4.8
Q6. Quality of NMR facilities	4.4
Q7. Quality of the sample preparation area and storage facilities	4.5
Q8. Ease of access to the facility out of hours	4.8
Q9. Your overall time at the facility	4.6
Q10. Arrangements for accessing data	4.5
Q11. Arrangements for returning any samples	4.6
Q12. Reimbursement of expenses	4.3

The raw questionnaire data is collected by the NRF administrator, with the process of extracting average scores and the compiling of comments checked by two members of the FE not at the host institution. The FE and the OC review the compiled questionnaire feedback at their six-monthly and annual meetings respectively, including also specific comments entered into free text boxes. We continue to be pleased with the very high feedback scores received, and the feedback provided is very helpful to the Local Management Team (LMT) to enhance the quality of the user experience.

9) Service Demand

*Please include a chart showing demand and capacity per month by year of operation of the current award.***

We report from July 2022 to June 2023 that corresponds to the six-monthly time-allocation rhythm of the high-field solid-state NMR NRF. We present information for the separate time-allocation periods and also for the separate 850 MHz and 1 GHz instruments.

The first table shows how the spectrometer time was used, in units of days.

Spectrometer time usage (% by day)	850 MHz July to Dec 2022	1 GHz July to Dec 2022	850 MHz Jan to Jun 2023	1 GHz Jan to Jun 2023
Time Allocation Panel allocated days	70% (129)	88% (161)	77% (139)	74% (134)
Fast Track	2% (3)	1% (1)		2% (3)
UKRI grant-funded days	4% (8)		3% (6)	1% (2)
PANACEA EU project	7% (13)	4% (7)	9% (17)	8% (14)
Industrial (Paid-for contract research)#		1% (1)		
Training (Connect NMR UK)				1% (1)
Facility manager research	11% (21)	2% (4)	8% (15)	10% (19)
Installation / calibration	1% (1)	3% (5)		
Maintenance	4% (7)	3% (5)	2% (4)	2% (3)
Compensation	1% (2)			
Spectrometer not usable				3% (5)
Total	184	184	181	181

#Johnson Matthey

We note the variation in FM research days, corresponding to 11% and 10% of total time on two occasions). Most of this FM research time is "to make the schedule work" (remembering the 365 days a year operation), e.g., when particular MAS probe(s) are out of action or a user's sample is not ready, or for days during holiday periods. As such, nearly all FM research is "short-notice" and often involves the FMT trying out things after experiments during a user visit were unsuccessful.

The below table shows an analysis for the TAP allocated days.

Service Demand (by day for TAP)	Total: 850 MHz & 1 GHz: July to Dec 2022		Total: 850 MHz & 1 GHz: Jan to June 2023		Total: 850 MHz & 1 GHz: July 2022 to June 2023	
TAP Applicant type	*requested*	*Actual days scheduled and used*	*requested*	*Actual days scheduled and used*	*requested*	*Actual days scheduled and used*
Outside Warwick (not Facility Executive)	176	145	236	194	412	339
Outside Warwick (Facility Executive)	55	48	52	48	107	96
Warwick (Facility Executive)	59	37	0	0	59	37
Warwick (not Facility Executive)	97	60	35	31	132	91
number of access days requested	387		323		710	
number of access days scheduled and used	290		273		568	

Note that by far the highest number of days in each time period (more than 50%) was for users who are neither from the host Institution or the five other Universities represented by the 8-person FE.

10) Risks

*Please include your risk register for the facility.** Provide a brief summary of how the risk register has been used during the reporting period and give examples of changes that have been made as a result.*

Review of the risk register is a standing item at each six-monthly FE and annual OC meetings. Changes compared to the risk register submitted in last year's report are highlighted in yellow. In particular, following a retirement, a new Deputy Director has been appointed and risk 2.4 from last year has been deleted as two new FE members have been added, so as to create more capacity and backup. A new risk 2.4 has been added due to the delay in confirming the process for renewal funding and the uncertainty this creates for people employed full time on the grant.

1. MOST SEVERE: Likelihood Low/ Impact High / Risk rating High

1.1 Catastrophic loss (e.g., due to fire) of the magnet hall(s)

Covered by university insurance, but both would require facilitating access to other instruments in the UK and overseas with FMT secondment, in person or online, to assist with remote experiments during rebuilding and re-equipping. Since the 850 MHz and 1 GHz instruments are housed in separate buildings, it would be hoped that damage could be contained to one of the two buildings should such a catastrophic event occur.

1.2 Quench of magnet

Mitigation: Bruker have a 24/7 active monitoring system, informing the LMT and Bruker, embedded into the magnet design and operational software. The construction of the new 1 GHz building lab has incorporated necessary venting and emergency hardware & pipework required for a quench situation. The magnets require regular top-ups of liquid helium (and also liquid nitrogen): Nitrogen is plentiful with many possible sources; Helium is much scarcer and we keep an eye on all suppliers and have a recovery system that has been in place at the University of Warwick Magnetic Resonance Laboratory since before the start of National Facility operation in 2010. (See also #3.2)

2. PERSONNEL: long-term unavailability of: Likelihood Medium/ Impact Medium / Risk rating Medium

~~The COVID pandemic increases the probability of personnel unavailability.~~ Risk of pandemic illnesses remains, but there is some cover built into the expanded team. The historical turnover of staff since the start of Facility operation (2010) or instances of absence are extremely low.

2.1 Director

The management of the NRF through the FE mitigates the impact if the Director is unavailable. A Deputy Director, Prof. Sharon Ashbrook (St Andrews), is in place along with the University of Warwick FE member, Prof Józef Lewandowski, who are empowered to act as required under the guidance of the FE to cover Warwick's formal legal responsibility as the grant holder.

2.2 FMT

The operation of the NRF is heavily reliant on the FMT. Under the current NRF funding, one Facility Manager is employed for each spectrometer, Dr Dinu Iuga and Dr Trent Franks for the 850 MHz and 1 GHz instruments. For covering short-term absence due to holiday and illness, the Facility Managers can cover for each other, though this significantly increases their workload during these periods. The University of Warwick local team supporting the Millburn House Magnetic Resonance Laboratory can provide support for more disruptive events, but the level of service provided to users would be significantly reduced. There is a risk of burnt-out among the FMT given the rapid change the NRF has experienced since 2020 with the doubling of the size of operation (with the 1 GHz instrument welcoming NRF users from 2021), and the relentless pressures of day-to-day operation that increased with COVID remote operation and subsequent changed user expectation. In principle, mitigation is for the FE together with the OC and the wider userbase, during the statement of need and NRF renewal process that is due to occur in 2023 and 2024 (though note #2.4 below), respectively, to consider carefully the appropriate staffing levels. Comparison should be made to similar NRFs and STFC facilities such as the Diamond synchrotron that offer (close to) equivalent 24/7, 365 days a year operation. Short-term mitigation through a one-year postdoctoral support post underwritten by the University of Warwick (after an unsuccessful application by the NRF in June 2023 to the EPSRC Living labs to improve the environmental sustainability of research infrastructure call), with partial funding from PANACEA. (The post is under offer for a July 2024 start.)

2.3 Administrator

Current processes are understood across the LMT as well as across the wider Physics Department administration team as a fail-safe.

2.4 Personnel insecurity due to uncertainty over follow-on funding

The delay in UKRI identifying the timescale and mechanism for applying for funding to continue NRF funding is starting to create real issues, with the highest potential impact through the insecurity for those staff fully employed on the delivering the service. Without timely reassurance over on-going employment, the potential for highly specialist staff to seek alternative employment increases. The FE will attempt to mitigate this through continued dialogue with UKRI colleagues to ensure a process for follow-on funding is identified at the earliest opportunity. Further mitigation is to look for what bridging funding may be possible from other sources if the retention situation looks serious.

~~2.4 Facility Executive~~

~~A reserve member named in the grant application, Prof. Yaroslav Khimyak, UEA, is in place.~~

3. EQUIPMENT FAILURE: Likelihood Medium-High / Impact Low-Medium / Risk rating Medium

3.1 Spectrometer Hardware

Manageable equipment failures during normal usage: duplication of equipment, notably probes, amplifiers, and pre-amplifiers; ability to carry out some in-house repairs, and close interaction with the suppliers.

3.2 Helium Supply Restrictions

Suppliers of liquid helium introduced rationing of supply in 2022. The NRF has been able to continue to fill its two NMR magnets thanks to the existing recovery of helium gas boil-off by means of a helium liquefier in the Department of Physics at the University of Warwick. EPSRC funding for the new 1.2 GHz system includes funding for an upgrade to recover helium also during magnet fills (this work should have been completed in 2023). A new risk is that the experienced engineer, Tom Orton (Physics, Warwick) who was undertaking this work and had oversight for maintaining the liquefier has left the University to take up a new position. The Department is currently clarifying how the helium liquefier is overseen, noting that the University has a maintenance contract with the vendor. A significant risk however is the age (approaching 20 years) of the helium liquefier and the NRF is actively involved in planning a replacement including a contribution to the cost of this in a future NRF funding bid.

[We note the feedback from the HLG on last year's report: "The HLG would like to know what % of recovery is acceptable. Also, if this a large value how you would plan for failure in local liquification facilities? Would you need distinct modular units for liquification to remove a single point of failure?" The Millburn House Magnetic Resonance Laboratory currently recovers ~two-thirds of the helium. The LMT and FE are considering options, in light of the NRF renewal, and are aware of the options for local liquification, that have been implemented, e.g., at the PANACEA site in Gothenburg, Sweden.]

4. VISITORS NOT ABLE TO VISIT IN PERSON: Likelihood Medium-High / Impact: Low-Medium / Risk rating: Low-Medium

In the event of restrictions to physical access to the laboratory (e.g. pandemics, transport and weather disruption), contingencies that proved themselves during the COVID-19 pandemic can be deployed to ensure a continuous operation of the NRF, namely the use of a) remote control operation of the facility by the experimenter & b) the use of the LMT to set up and monitor the experiments on behalf of the experimenter within the lab. Given the experience of COVID-19 we would seek to classify the local team as 'essential' worker in the event of a 'hard' lockdown allowing them to keep the service running. This approach was successfully used by several universities in 2020.

Following the pandemic, the option to use the facility remotely was adopted as a value added standard procedure as it gives greater flexibility to the teams who use the facility to run their experiments (but note the effect this has on point 2.2 above).

5. HIGH INFLATION ENVIRONMENT PUTS PRESSURE ON RUNNING COSTS: Likelihood High / Impact: Low-Medium / Risk rating: Low-Medium

After years of a relatively stable cost environment (with the exception of helium inflation) there is now high general inflation. This could have a significant effect on the running costs and of being able to upgrade equipment to keep it leading-edge. The FE keeps the budget under regular review and if the pressure mounts think about what cost savings can be made to protect the continuing provision of high-field solid-state NMR access to users.

This is also relevant for costs set by key suppliers, notably Bruker, where there is a significant risk that very high repair costs could mean that it is not affordable to repair equipment, meaning that science research cannot occur.

6. LOWER THAN TARGETTED COST RECOVERY: Likelihood Medium-High / Impact: Medium / Risk rating: Medium

The NRF has a cost recovery target associated with its funding as an EPSRC NRF: for 2024, this is 20% of costs (associated with 60% FEC funding from EPSRC). The NRF seeks to recover this from funded days for grants submitted by users and paid-for industry usage. As of 2023, both sources are below the required break-even point. While the financial loss can be funded by the host and partner universities, there is a reputational risk to the NRF, in particular as expressed in evaluation of the NRF's annual report by the EPSRC panel. (In this report, mitigation measures taken by the FE are discussed in section #6.)

11) Key Performance Indicators (KPIs) and Service Level (SLs) (max. 2 pages)

For the reporting period, please provide brief evidence of the facility's performance against its Key Performance Indicators and Service Levels. This information should be tabulated where possible, with a Red/Amber/Green rating, and include the following information:

- *Brief description of each KPI or SL;***
- *Information or data associated with the facility's actual performance against each KPI or SL during this reporting period;*
- *Target metric for each KPI or SL.***

For any targets that were not met, please provide detail and describe the steps taken to mitigate negative impact on users and measures taken to improve performance. Often how an issue is dealt with is more positive information for the HLG.

July 22 to June 23		Replied within 5 working days	% Replied within 5 working days
Inquiries to LMT from new or not regular academic users	9	9	100%
Inquiries to LMT from new or not regular industry users	3	3	100%
Fast-track applications by existing users	0		N/A
Fast-track applications by new users	3	3	100%

PhD travel fund applications	4	4	100%

TIME ALLOCATION CALLS Jul 22 – Jun 23	Round 27 (Oct 31st 2022 deadline, 850 MHz & 1 GHz for Jan to June 2023)	Round 28 (April 30th 2023 deadline, 850 MHz & 1 GHz for July to Dec 2023)	Combined
number of access days requested	323	296	619
number of access days awarded	256 + 37 reserve	249 + 35 reserve	505 +72 reserve
% of access requests responded to within 10 wds of TAP	100%	100%	100%
number of distinct PIs	22	18	27
number of distinct universities	14	11	15
Department type (of each distinct PI)			
Chemistry	8	7	10
Physics	3	3	5
Engineering (including Chemical or Mechanical Engineering)	3	3	4
Biological or Life Sciences	3	2	3
Biochemistry	1	1	1
Materials	3	1	3
Pharmacy	1	1	1
USERBASE DIVERSIFICATION			
The NRF will report the number of new PIs applying to the facility and their research backgrounds (subject field, current expertise in solid-state NMR or not). Data reported biannually after each TAP meeting.	1 in Physics (solid-state NMR expert), 2 in Chemistry, and Materials Science & Engineering (not solid-state NMR experts)		

We note that, for the two TAP rounds in this reporting period, the NRF is back to the case of overdemand, as had always been the case prior to COVID.

DOWNTIME				
Percentage downtime: <10%, >10% but < 20%, >20%	2022		2023	
Downtime KPI: Percentage downtime over period. Report reasons for downtime, Data reported every 6 months.	850 MHz, July to Dec (184 days)	1 GHz, July to Dec (184 days)	850 MHz, Jan to June (181 days)	1 GHz, Jan to June (181 days)

maintenance days	7	4%	5	3%	4	2%	3	2%
user granted a compensation day	2	1%		%		%		%
Spectrometer Down		%		%		%	5	3%
Total	9	5%	5	3%	4	2%	8	4%
engineer installation days (not counted as downtime)	1 (1%)		5 (3%)					

COMPLAINTS		
Complaints: The NRF will report the number of user complaints and response times. Data reported every 6 months.	Number of Complaints	First response within 3 working days and full response within 10 working days
3 working days for first response, 10 working days to resolve the issue: 95% and above; >90% but < 95%; <90%	0	N/A
USER SATISFACTION		
USER SATISFACTION SCORES: 4; 3; 2	Number:	Average score
PI Survey (2022)	28 sent, 22 received	4.7
Visitor Survey (July 22-June 23)	43 sent, 22 received	4.6

DISSEMINATION EVENTS		
Perform a minimum of one dissemination activity per year	Connect NMR UK workshop (in-person, 28th March 2023) and Annual Symposium (hybrid in-person & online, 29th March 2023)	
	July to Dec 22	Jan to June 23
New snapshot videos hosted on YouTube	1	0
Number of followers of Twitter account	484	571
Information emails sent by the Facility to mailing list	1	2

PUBLICATIONS	
The NRF will report the numbers of publications acknowledging the Facility. Data reported annually.	
KPI Number of outputs 15; 12; 10	15 (2022)

RESEARCH OUTPUTS (TALKS & POSTERS)	
Number of Research Outputs, including talks, posters etc. Data reported annually.	
KPI Number of outputs 50; 30; 20	54 (2022)
OUTREACH TO A WIDER AUDIENCE	
Number of distinct non-NMR meetings at which research outputs are presented by users. Data reported annually.	
KPI Number of outputs 15; 12; 10	20 (2022)
GRANT APPLICATIONS FOR ACCESS	
Number of PIs submitting grant applications for access for which the Facility has provided a technical assessment. Data reported annually	
KPI Number of applications 8; 6; 4	5 (2022)

We note the low number of grant applications in 2022. However, this does seem to be an anomaly, given that 2023 by comparison saw the highest ever number (since 2016) of 14 applications for 485 days (compared to 5 applications for 49 days in 2022 and 11 applications for 261 days in 2021). However, note the mitigation taken by the FE, as discussed in #6 and #10.

Note that the talks and posters KPIs are back in green in 2022, corresponding to the restart of in-person conferences. The topics of the distinct non-NMR meetings at which research outputs are presented by users are stated in #12.

12) Links

*Include description of new links made and how existing links have been strengthened during the reporting period. What links does the facility have with other NRFs, institutes, Diamond etc?** What international links does the facility have.** What plans does the facility have to maintain, increase and strengthen such links? If your facility is based outside of the UK how is this a strength of the facility?***

The capability and outputs of the NRF are at the cutting edge and are well-known internationally. Population of the external governance structure (see #14) ensures direct input from leading overseas solid-state NMR centres (MIT, USA and CEMHTI, Orleans, France), as well as a solid-state NMR spectroscopist from UK industry (Johnson Matthey). The external input extends to other techniques and leading UK facilities, e.g. the Diamond synchrotron, and SUPERSTEM. The facility has links with other scientific bodies aimed at promoting the application of cutting-edge solid-state NMR methods for elucidation of structure of advanced materials (several members of the FE have active roles in the Collaborative Computational Project for NMR crystallography (CCP-NC) and NMR Crystallography Commission of the International Union of Crystallography).

The FMT have initiated a new forum for local operators of high-field NMR facilities, organising a first online meeting in November 2023 with 22 attendees from 12 1+ GHz sites in Canada, France, Germany, the Netherlands, the UK, and the US. A follow-on meeting is planned in 6 months time.

The UK High-Field Solid-State NMR Facility well integrated within the EPSRC-funded Connect NMR UK network (https://www.connectnmruk.ac.uk/) In continuation from 2022, the NRF partnered with Connect NMR UK network to run a training workshop for NMR scientists with no or very little solid-state NMR experience, the day before the NRF annual symposium on 27th March 2023 (see #5).

The outreach to other research communities included a presentation by the Technical Director at the Institute of Physics Condensed Matter and Quantum Materials meeting in Birmingham, June 2023. Noting the feedback on last year's report: "*The NRF should consider synergy with other NRFs regarding material research, such as EMFL and EPR,*" the Directors of the solid-state NMR and EPR NRFs gave talks at a one-day meeting in Oxford (December 2023), entitled Science and Technologies in High Magnetic Fields, and co-organised by the EMFL NRF Director. One of the NRF's KPIs (see #11) is "Number of distinct non-NMR meetings at which research outputs are presented by users": topics of these conferences for 2022 and 2023 include: Battery Materials, Cancer Precession Medicine, Catalysis, Cellulose, Chemistry of Cement, Condensed Matter, Crystallography, Electrochemistry, Fast-ion Conduction in Solid Electrolytes, Glass Technology, Hybrid and Organic Photovoltaics, Lithium Batteries, Materials Science, MOFs, Perovskite Solar Cells and Optoelectronics, Pharmaceutics, Physics of Non-Crystalline Solids, Plant Cell Walls, Polysaccharides, Porous Materials, Solid-State Chemistry.

The NRF instrumentation at 850 MHz and 1 GHz are also now integrated into the PANACEA project, A Pan-European solid-state NMR Infrastructure for Chemistry-Enabling Access (https://panacea-nmr.eu/), that started in September 2021 with funding from the European Union Horizon 2020 INFRAIA-02-2020: Integrating Activities for Starting Communities call. This 4-year €5M initiative links together high-field solid-state NMR laboratories in Europe (Denmark, France, Italy, the Netherlands, Portugal, Sweden, Switzerland and the UK) as well as the National High-Field Magnet Laboratory in the USA The PANACEA project envisages visitors from other European countries using the 850 MHz and 1 GHz spectrometers for a total of 96 days. To date, 61 days of NMR time at 850 MHz and 1 GHz have been allocated to PANACEA projects and visitors from Italy, Poland, Romania and UK have used the NRF (see also #7). Dr Trent Franks gave a presentation on "*Fast spinning experiments at the UK SSNMR NRF at University of Warwick*" at the PANACEA meeting in Florence (November 2023). Links to the US National High Magnetic Field Laboratory (NHMFL) in Florida have been strengthened by a joint project led by the Technical Director, to access specialist hardware for a collaborative project on ^{67}Zn NMR (visited in October 2023).

The NRF is also represented, with the University of Warwick one of 26 partners, within the REMOTE NMR (R-NMR): Moving NMR Infrastructures to Remote Access Capabilities 3-year €1.5M project (https://r-nmr.eu/) that started in July 2022 with funding from the HORIZON-INFRA-2021-DEV-01 call. Dr Trent Franks gave an online presentation at the R-NMR Remote Access Workshop in June 2023 titled 'Remote Access NMR: Experiences from a National Solid-State NMR Facility'. Dr Franks also gave a talk at the University of Warwick Facilities Roadshow: "*Solid-State NMR capabilities at the University of Warwick*" (June 2023).

13) Improvements and future plans

Please indicate steps that have been taken to improve the access, user experience and ensure the long term sustainability of the facility. This can include plans for achieving ISO accreditation, any proposed equipment upgrades, user training and staff training etc.

The NRF continues to focus on ensuring that it provides the research community with access to state-of-the-art infrastructure and training for its users. Over the last year, the NRF has continued work towards the installation of the 1.2 GHz solution-/solid-state NMR spectrometer, whilst ensuring that user receive access to high-quality instrumentation at 850 MHz and 1 GHz. The ability to develop this new capability whilst maintaining the high-quality support users expect has frequently placed large demands on the LMT. The new 1.2 GHz spectrometer, which will ensure that the UK research community acquires access to the highest commercially available NMR instrumentation, will amplify the challenges. Solution- and solid-state NMR probes have been ordered from Bruker and Phoenix, such that they will maximise the potential user base and ensure that the community, has access to as broad a range of experiments as possible. The probes include both 3 and 5 mm liquid-state cryoprobes, and a range of solid-state magic-angle spinning probes that will allow access to a broad range of nuclei and offer spinning frequencies of up to 111 kHz. During the year, the first quarterly meetings between the NRF and the 1.2 GHz site in Birmingham took place with the representatives from the user community of each. In January 2024, the first high-level 1.2 GHz oversight group meeting took place in Birmingham with participation by UK scientists from the physical and life sciences, as well as representatives from BBSRC, EPSRC and MRC (See #5 for a description of the 1.2 GHz industry group). These initiatives will aid in the development of the instrumentation and ensure that investment is complementary.

With funding from the EPSRC Core Equipment Grant (EP/V03622X/1) we have also been able to enhance the capabilities of our existing instruments and improve the environment for sample preparation. To further enhance the range of temperatures over which we can conduct solid-state NMR experiments, a low-temperature cabinet and low-temperature 1.9 mm magic-angle spinning probe were ordered. This probe extends the temperature range at which measurements can be conducted down to 100 K. This instrumentation complements a recently commissioned laser probe, ensuring that users can now collect data from 100 to 1000 K.

Support from the EPSRC Core Equipment Grant (EP/V03622X/1) also ensured that we were able to enhance sample packing capabilities. The installation of an ultracentrifuge equipped with swing out rotor and inserts permits the pelleting of samples directly into the magic-angle spinning rotor. In addition to minimising sample losses and denaturation, this instrumentation opens up the possibility of conducting sedimentation NMR studies, extending the range of samples that can be studied to large macromolecular complexes such as viruses and non-membranous organelles.

The NRF participated in the EPSRC Research Infrastructure EDI Survey (April 2023). In response to feedback from the OC, the LMT revised the format of the Excel file summarising applications that is used during the TAP, namely, PI names were hidden and the order in which proposals were discussed was randomised (whereas previously applications had always been considered in alphabetical order of the PI).

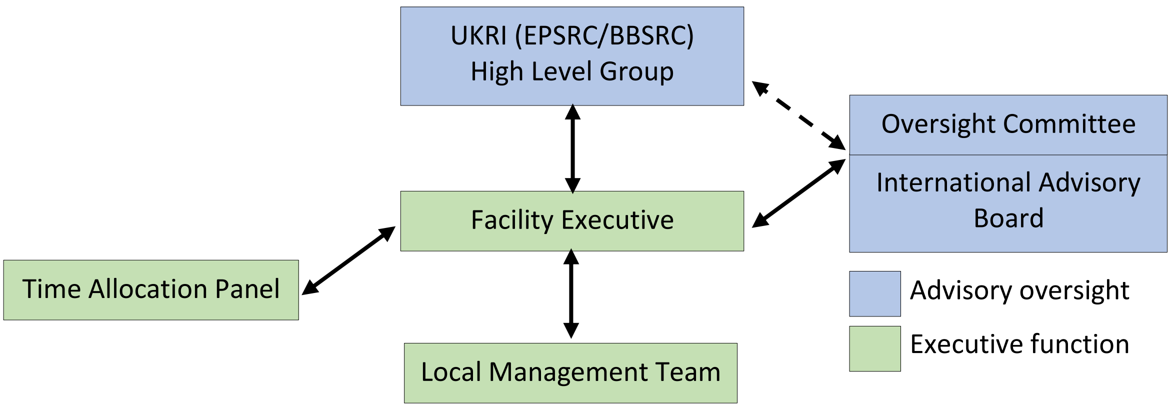
Over the last year, we have also been proactive in engaging with the wider ultra-high field community. In October 2023, the Technical Director has visited the NHFML in Florida to learn about the design and construction of probes for ultra-high fields as well as to share best practice as to how the laboratories are managed for the user community. To build on such initiatives, an application has been made to the EPSRC to establish a centre-to-centre collaborative network between ultra-high field labs to push the limits of high-field solid-state NMR technology, allowing best practice to be shared between the world’s leading solid-state NMR labs to bring advances in areas including material science, pharmaceuticals and life sciences. In addition, see in #12 about the forum for local operators of high-field NMR facilities.

The FE held a specifically convened strategy session (May 23) in addition to its usual meetings to create the space to allow thinking around the medium-term to include how the 1.2 GHz instrument needs to be integrated, especially with the remit expanding to include solution-state work. Issues looked at as the scale of the Facility increases included what are the most efficient approaches to staffing it and providing support, as well as thinking about the nature of the capability required of a leading-edge NMR facility in the medium term. Four early career academics not on the FE (from Birmingham, Cambridge, Manchester and Warwick) were invited to join the session to give their perspectives.

The key staff employed full time by the Facility (Technical Director, Facility Manager) now have more career development opportunities through the creation of a new technical specialists promotion pathway at Warwick.

14) Governance structure

Please provide a chart to illustrate the governance structure of the facility, including details of your steering committee/advisory board membership, their roles e.g., user representative, instrument representative etc. How does the facility work with its steering committee and/or external advisory board? Please provide information on any changes to the governance structure during the reporting period.



Oversight Committee
Prof. R. Brydson (Chair, NRF)
Dr S. Day (industry)
Dr J. Parker (DLS)
Dr G. Rees (User representative)
International Advisory Board
Dr P. Florian (replacing Dr. A. Lesage)
Prof. M. Hong

Local Management Team
Prof. S. Brown (Director)
Dr D. Iuga (Technical Director)
Dr T. Franks
Mr C. Westwood

Time Allocation Panel
Prof. J. Griffin (Chair)
Dr D. Kubicki
Dr L. Costanar Acedo

Facility Executive
Prof. S. Brown (Director)
Prof. S. Ashbrook (Deputy Director)
Prof. M.E. Smith
Prof. P. Williamson
Prof. J. Lewandowski
Prof. F. Blanc
Prof. J. Griffin
Prof. Y. Khmak
Dr W. Chow

The diagram above shows the governance structure which balances the internal checks and support of the management and executive function with the completely external scrutiny providing non-executive oversight and expert advice. The website gives the detailed terms of reference and remits of these bodies. There are three executive committees. The Local Management Team (LMT) effectively run the facility on a day-to-day basis under delegated authority from the Facility Executive (FE) which has ultimate responsibility for delivery of the service against its KPIs, along with determining its strategic direction and development as an internationally-leading facility. With the expansion of the Facility in recent years, the high level scientific support in the Facility Management Team (FMT) within the LMT has been extended to two facility managers (Iuga, Franks). The FE comprises a complementary group of UK solid-state NMR spectroscopists with expertise that cover all the key areas of research the Facility undertakes. The governance structure means while the LMT operates with a high degree of autonomy; it reports all substantial actions to the biannual full meeting of the FE, also taking advantage of the electronic communication for FE input into any substantial decisions between meetings. Time allocation is a further delegation where separation of responsibilities occurs from both the LMT and FE in deciding which experiments are recommended for a time allocation on the Facility. To allow connectivity to the FE, a non-Warwick member of the FE chairs the Time Allocation Panel (TAP) on an annually rotating basis, with two completely external expert members who are rotated biennial, but in a sequential manner (i.e., so that there are always two TAP members with experience of one or more previous TAP meetings). There is well defined complaints procedure which follows best practice, initially trying to resolve the complaint informally, with an escalation procedure to the full FE and ultimately to the Oversight Committee (OC). The user questionnaires are scrutinised by a designated member(s) of the FE who is not from the LMT and any issues are highlighted at the FE meetings. To improve the effectiveness of the FE meetings, a separate technical issues meeting has been set up (to meet every 3 months) under the auspices of the FE, but with a subset of the FE. Part of the meeting directly involving the manufacturers to improve mutual understanding in dealing with key issues.

Advisory oversight is formally provided through the annual report to UKRI which is scrutinised by the High Level Group. The views fed back are discussed by the FE as well as being a key input into the meeting with OC. The OC has expertise in running facilities as well as providing a user voice and an industrial user perspective. The International Advisory Board provides expert international solid-state NMR input to allow the OC to really be able to benchmark performance of the Facility and to catalyse strategic discussion about the further development of the Facility. The OC/IAB are used to scrutinise nominations for appointments before recommendation to UKRI. This provides confidence to UKRI of the quality and complementarity of the nominations being made. There have been no changes made to the governance structure this year, other than changes of personnel populating some of these committees through natural turnover and retirements.

Any comments on the facility from your advisory board:

The latest annual meeting with the OC/IAB was on 29/03/23 which was held in hybrid form. Scrutiny of the KPIs showed that in general these were mostly very well met and exceeded, which the OC commended. Three issues noted were (i) the relatively low number of industrial users, (ii) recovery of costs from grant funding to make the Facility to make it financially sustainable, and (iii) the increasing burden on local personnel with the increasing number of new users along with the increasing complexity of the Facility and the age of some of the infrastructure. All these points are recognised by the FE, particularly for the cost recovery from grants applications. The FE considered a detailed paper at its October 2023 meeting (outside the window requested here so will be dealt with next year). There was some concern from the OC that the annual report was becoming longer such that UKRI should reflect on the burden they were placing on NRFs which seemed counter to some recommendations in recent reviews. In the interest of transparency there should be more opportunity for the NRFs to meet directly with the High Level Group. There was agreement that with the addition of the 1 GHz careful consideration of a realistic target KPI for publications under a two-instrument set up should be considered. It was agreed the KPI related to the number of emails managed was now much less relevant and should be dropped. The User Representative noted the user questionnaires are generally very positive and this was commended by the OC. One issue identified is the adequacy of the sample preparation facilities especially with the increasing volume of work. The FE are looking at this carefully as the Facility expands. Also applicants would welcome more detailed feedback from the TAP especially when the time allocation is cut and it was agreed this would be looked at.

Please provide your advisory board with the opportunity to include any comments they have on the facility, which they wish to include in this annual report.

15) Website (this section will be taken into account but not individually scored)

*Please include a link to your website.** What changes have been made during the reporting period? What plans do you have to develop this space and what web analytics data do you have from visits?*

Website and Social Media Platforms

[The UK High-Field Solid-State NMR Facility (warwick.ac.uk)]()

[The UK High-Field Solid-State NMR Facility - YouTube]()

The UK High-Field Solid-State NMR Facility (@NrfHf) on Twitter (since October 2020).

The main website is used as both an information resource hub for new and established users as well as an administration tool for the LMT.

Engineering and Physical Sciences Research Council

Outreach Analytics

Website Hits (July 2022 – Dec 2022)

July - Dec 2022	Total Hits	On-Campus Hits	External Hits	Student Hits	Distinct IP addresses
July	1299	57	1242	2	1135
Aug	1401	46	1355	3	1254
Sept	1234	78	1156	3	1057
Oct	2242	137	2105	11	1872
Nov	1421	92	1329	1	1217
Dec	1971	43	1928	0	1690

Website Hits (Jan 2023 – June 2023)

Jan - Jun 2023	Total Hits	On-Campus Hits	External Hits	Student Hits	Distinct IP addresses
Jan	1804	74	1730	7	1496
Feb	1686	115	1571	4	1420
Mar	2936	163	2773	2	2274
Apr	1484	104	1380	1	1230
May	1522	83	1437	9	1201
Jun	1046	79	967	3	854

Top Website Pages (July 2022 – June 2023)

Page name	**Hits**
National Research Facility	4566
The Symposium 2023	1566
Call for Applications	509
850 MHz Probes	431
Annual symposia	407
Publications	383
1 GHz Probes	369
People (Local Management Team)	218
The Symposium 2022	215
Applications for access	213
UK Solid-State NMR	199
NRF Pre-schedule check-in	184

Expense Claim	173
User Report	157
Online application form	149
Fast track applications	142
Travel fund	138
Publicity	124
Project Visitor Declaration	111
Contact	108

The UK High-Field Solid-State NMR Facility - YouTube
6 snapshot videos currently uploaded onto the channel.
(1) Tracking Defects by MAS NMR. Presenter: Prof. Frédéric Blanc, University of Liverpool
(2) Research from Phys. Chem. Chem. Phys., 2020, 22, 14514 - 14526. Presenters: Zachary Davies and Cameron Rice, University of St Andrews.
(3) Oxygen-17 NMR: Prof. Frédéric Blanc, University of Liverpool
(4) Gain structural insight from ^{27}Al. Presenter: Dr Valerie Seymour, Lancaster University.
(5) The use of the NMR facility to study magnesium acetate. Presenter: Dr Valerie Seymour, Lancaster University.
(6) ^{14}N–^{1}H HMQC solid-state NMR as a powerful tool to study amorphous formulations – an exemplary study of paclitaxel loaded polymer micelles. Presenter: Prof. Ann-Christin Pöppler, University of Würzburg, Germany (research with the NRF Director, Prof. Steven Brown, Warwick).

Title	Views	Watch time (hours)	impressions
Total	88	1.1	697
Snapshot Video 1	10	0.2	46
Snapshot Video 2	14	0.3	51
Snapshot Video 3	13	0.1	45
Snapshot Video 4	13	0.1	71
Snapshot Video 5	8	0.1	28
Snapshot Video 6	30	0.3	456

The UK High-Field Solid-State NMR Facility (@NrfHf) / X (Twitter) (598 followers)

2022	July	Aug	Sept	Oct	Nov	Dec
Tweet impressions	376	435	357	7048[a]	428	380
New followers	4	15	4	20	12	7

[a]The much higher number in October 2022 corresponds to the announcement of the award of £17M by UKRI for 1.2 GHz NMR.

2023	Jan	Feb	Mar	Apr	May	Jun
Tweet impressions	1409	1549	2614	190	2875	1760
Profile visits	114	168	111	[a]	172	63
New followers	23	20	25	13	10	13

[a]Information not provided by X analytics.

16) Additional information (optional, max 1 page) (this section will not be scored)

You may use this section to include any additional information that you would wish the HLG to receive.

We note the high reporting demand placed on the NRF to prepare this annual review that, including the three case studies, exceeds 40 pages.

We would prefer for the reporting period to switch to a calendar year, i.e., January to December.

1. Title of Case Study: High-Field Solid-State NMR for the Study of Optoelectronic Materials

2. Grant Reference Number: EPSRC EP/M028186/1, EP/K024418/1, EP/T015063/1, EP/R029946/1

3. One sentence summary: Multinuclear high-field solid-state NMR provides insight into the local structure and disorder of materials for optoelectronic applications.

One paragraph summary: Optoelectronic materials are important for the development of devices that transmit, convert or emit light energy with increased efficiency. In many cases, they feature highly complex structures or display intrinsic disorder or dynamics. Diffraction and electronic measurements can provide insight into the long-range structure and transport properties, and solid-state NMR can complement this by providing detailed information on local structure, dopants and substituents, which are often critical to the material properties. This case study highlights the advantages of high-field solid-state NMR for such studies and the detailed structural information that can be obtained.

5. Key outputs in bullet points:

- *Atomic-level structural insight into complex optoelectronic materials*
- *International research collaborations supported by the NRF*
- *Complementarity of high-field NMR with other advanced characterisation techniques*
- *Observation of challenging nuclei and thin film samples*

6. Main body text: Optoelectronic materials are an important class of materials with applications including photovoltaics, low energy light emission and sensing. One class of materials that have received intense interest over the last 10 years is hybrid perovskites, which show extremely high solar cell efficiencies exceeding 25%. The perovskite structure is based on organic cations within a metal halide framework. In addition to the intrinsically high charge carrier diffusion lengths, the multi-component hybrid structure offers high chemical versatility, allowing the band gap to be tuned towards particular applications. Despite the intense interest in these materials and the rapid development into what is now a mature research field, many aspects of the structure-property relationships remain poorly understood. One challenge in mixed composition hybrid perovskites is the presence of intrinsic and light-induced phase segregation which can be detrimental to the efficiency and stability. Recently, it has been found that doping a caesium cation sublattice with rubidium can suppress phase segregation in mixed halide perovskites. Wang *et al*. used ^{133}Cs and ^{87}Rb MAS NMR measurements at 20 T to study the cation speciation within these materials. The increased chemical shift resolution at high field made it possible to identify distinct Cs environments in single halide end members, whereas broadened lineshapes in a mixed halide I/Br compositions confirmed that all Cs was incorporated within the same phase. Viewing the same materials from the perspective of ^{87}Rb NMR also confirmed that Rb cation dopants up to the studied level of 10% were fully incorporated into the Cs sublattice, supporting that the incorporation of lattice strain helps to suppress phase segregation.

Another strategy for increasing the stability of hybrid perovskites is to incorporate bulky cations to form two-dimensional structures. However, due to reduced electron mobility, these 2D structures must be aligned to maximise efficiency. Lehner *et al*. used ^{13}C MAS and CPMAS NMR at 20 T as part of a study of preferential alignment in ultrathin perovskite films containing 3-fluorobenzylammonium (3FBA) cations. Here, the high magnetic field was essential to maximise the sensitivity of the dilute ^{13}C nucleus within the small sample volumes studied. The increased chemical shift resolution also helped to identify subtle differences in aromatic region, indicating that indicating the conformation of 3FBA adapts depending on the number of surrounding 3D slabs in the structure. In a separate study, Lekina *et al*. used ^{1}H MAS NMR at 23.5 T to characterise the dynamics of bulky hexadecylammonium (HDA) cations within a lead iodide perovskite lattice. Exploiting the increased resolution under fast MAS conditions at this magnetic field, it was possible to individually measure ^{1}H T_1 relaxation constants for protons at different positions along the HDA alkyl chain. The relaxation times exhibited substantial variation whereby T_1 increased with increasing distance from the NH_3^+ head group. This indicates that aliphatic protons close to the NH_3^+ are more mobile and dynamic than the more rigid hydrophobic portion of the HDA chain.

Vashishtha *et al*. used ^{39}K MAS NMR at 20 T to provide insight into the local structure in a series of K-substituted $Cs_2AgInCl_6$ double perovskite nanocrystals. Owing to its low gyromagnetic ratio, ^{39}K is extremely challenging to observe, particularly in the presence of broadening due to disorder. By maximising the sensitivity at high magnetic field, it was possible to obtain ^{39}K MAS NMR spectra in the presence of extensive structural disorder, allowing distinct environments for K^+ substituted onto A and B sites within the perovskite structure to be identified and correlated with DFT-calculated chemical ranges. An important observation from this work is the pronounced changes in proportions of the different local environments as the K substitution level is varied, whereby the specific composition of 60% K provides an optimal balance between covalent character, restricted Cs^+ mobility and K^+ incorporation into the perovskite structure.

Another class of materials that display promising optical properties are tellurite glasses. These materials exhibit higher refractive indices, lower phonon energies, and increased infrared (IR) transmittance than silica glasses, making them promising candidates for optical applications in the near- and mid-IR. Network modifiers such as alumina are often used to increase the thermal stability and durability of tellurite glasses; however, the interdependence of glass composition, structure, and functional properties is not fully understood. Barney *et al*. used ^{27}Al MAS NMR at 20 T to probe the local Al environments in a series of series of Al_2O_3-TeO_2 glasses with compositions up to 16 mol% Al_2O_3. The spectra enabled observation and quantification of distinct AlO_4, AlO_5 and AlO_6 environments in the structure, with the high magnetic field critical for the observation of AlO_5 environments which typically exhibit large quadrupolar interactions owing to the less symmetric bonding environment. The increased sensitivity and reduction of ^{27}Al quadrupolar interactions at high field also enabled a ^{27}Al double-quantum (DQ) dipolar correlation spectrum to be obtained, which provides direct insight into relative Al – Al proximities in the structure. This revealed a strong clustering of like pairs of AlO_6 and AlO_4 but not AlO_5, despite the clear presence of these in the one-dimensional spectrum. Modelling the DQ build up with spin simulations enabled a quantitative model for AlO_n distances in the structure to be obtained.

Wang *et al*., *Nature* 2023, 618, 74; Lehner *et al*., *Adv. Mater.* 2022, 35, 2208061; Lekina *et al*., *J. Phys. Chem. C* 2023, 127, 33; Vashishtha *et al*., *J. Mater. Chem. A* 2022, 10, 3562; Barney *et al*. *J. Phys. Chem. C* 2020, 124, 37.

7. Names of key academics and any collaborators:

Dr Dominik Kubicki (University of Birmingham), Prof. Martin Kaltenbrunner (University of Linz), Prof. Edward Sargent (University of Toronto), Prof. John Hanna (University of Warwick / Nanyang Technological University), Prof. Shen ZeXiang (Nanyang Technological University), Dr Parth Vashishtha (Nanyang Technological University), Dr Emma Barney (University of Nottingham), Prof. Ray Dupree (University of Warwick)

8. Sources of significant sponsorship (if applicable):

EPSRC (and BBSRC) funding for the UK High-Field Solid-State Nuclear Magnetic Resonance Facility

9. Who should we contact for more information?

Prof. John Griffin, Lancaster University, j.griffin@lancaster.ac.uk

1. Title of Case Study: NMR Studies of Soft Matter

2. Grant Reference Number: EP/P019943/1, EP/N033337/1, BB/X011054/1

3. One sentence summary: ^{1}H, ^{13}C and ^{19}F NMR spectra obtained at the UK High-Field Solid-State NMR National Research Facility provide structural and dynamic insight into the organisation of soft-matter systems where domains with different ordering and dynamic states coexist in complex multiphase assemblies such as hydrogels, liposomes and plant-based biomaterials.

4. One paragraph summary:

NMR spectroscopy is a powerful analytical tool for characterising the structure of molecules and materials with atomic resolution via the local magnetic interactions that are sensitive to the local electronic environment of the atomic nucleus as well as dipolar and J couplings of nuclear spins that inform on through-space proximities and through-bond connectivities. For soft matter systems, the usual challenges of solid-state NMR spectroscopy related to the need of averaging out anisotropic magnetic interactions via magic-angle spinning (MAS) are amplified by the technical demands of using MAS on multiphasic materials and the very much reduced sensitivity due to very high content of a solvent or other phase-forming species (e.g., lipids in liposomes). This case study describes the application of combined solid- and solution-state advanced NMR tools to characterise different aspects of the structure, dynamics and interfacial connectivities in soft matter systems, benefitting from the enhanced resolution and sensitivity provided by working at the high magnetic fields of the UK High-Field MHz Solid-State NMR National Research Facility (NRF). By combining NMR findings with the data from other advanced characterisation tools that probe structure and dynamics in these systems at different length and time scales, a generic tool-kit of methods for assessing the structure and interface interactions in very challenging soft matter systems has been developed. Such fine detail in structural analysis is of importance for the development of soft matter systems for applications in different fields encompassing pharmaceuticals, biomaterials, food and home-care industries.

5. Key outputs in bullet points:

- *A generic tool-kit of solid- and solution-state NMR methods for assessing molecular-level organisation and interface connectivities suitable for studies of different classes of soft matter systems.*
- *Molecular-level understanding of key interfacial interactions that govern the formation of metastable soft-matter materials; this insight is critical information for directing industrially relevant applications of such materials in different fields.*
- *Use of NMR crystallography (comparison of experiment to NMR chemical shifts and quadrupolar parameters calculated using density-functional theory) in combination with solution-state NMR to quantify the effect of specific key intermolecular interactions on the self-assembly of molecular soft-matter systems.*

6. Main body text

NMR characterisation of soft matter systems relies on the combined application of advanced solid- and solution-state NMR focussing on the rigid and mobile constituents, respectively, in these complex heterogeneous structures. NMR characterisation has been performed at a magnetic field strength of 20 Tesla (corresponding to a ^{1}H Larmor frequency of 850 MHz) in projects of relevance to Unilever, Croda and Iceni Diagnostics.

^{19}F NMR provided the benefit of enhanced sensitivity of particular importance for detecting gelators or guest molecules that are distributed between different compartments of soft-matter systems.

Williamson et al. have developed a ^{19}F solid-state MAS NMR methodology to determine the partitioning of these (non-UV-active) compounds into lipid vesicles without the need for separation of the vesicles. The method utilizes ^{19}F MAS NMR to quantitatively characterise the partitioning of the fluorinated compounds between the aqueous and membrane phases. Khimyak et al. used combined solid- and solution-state NMR ^{13}C, ^{19}F, ^{13}C-^{19}F and ^{1}H based methods to identify enzymatically produced nanofibers due to a new allomorph of cellulose and to assess the effect of introducing of ^{19}F labels on the local ordering, both in the bulk and at the surfaces of such assemblies.
A similar combination of ^{13}C and ^{1}H solution- and solid-state NMR methods enabled Khimyak et al. to characterize the structure of bacterial cellulose (BC) ribbons at ultra-high resolution and to monitor the local mobility and water interactions in the hydrogels obtained in the presence of the "guest" glucans, thus identifying their effect on the short-range order, mobility, and hydration of BC fibres.
Warren and Khimyak et al. employed a range of NMR methodologies enabling simultaneous detection of mobile and rigid components and water/carbohydrate interactions to probe the molecular mobility and water dynamics in starch hydrogels featuring a wide range of physical properties. The presence of highly dynamic starch chains, behaving as solvated moieties existing in the liquid component of hydrogel systems was correlated to their macroscopic and biochemical properties, thus facilitating the tailored study and design of novel, environmentally friendly soft matter biomaterials for future use.
By employing a combined solution- and solid-state NMR approach for the study of the assembly of G-quadruplexes, Brown et al. identified the crucial role played by solvent effects and ion concentration on the structural integrity, and hence functionality of G-quadruplexes in the solid state as compared to in solution. Distinct N-H···N and N-H···O intermolecular hydrogen bonding interactions drive quartet and ribbon-like self-assembly resulting in markedly different 2D ^{1}H solid-state NMR spectra, thus facilitating direct identification of mixed assemblies.

References:
Williamson et al, Angew. Chem. Int.Ed. 2023, 62, e202301077; DOI: doi.org/10.1002/anie.202301077
Khimyak et al, Chem. Eur. J. 2021, 27, 1374 –1382, 2021 DOI: 10.1002/chem.202003604
Khimyak et al, Biomacromolecules 2019, 20, 4180-4190 DOI: 10.1021/acs.biomac.9b01070
Khimyak, Warren et al, Carbohydrate Polym. 2020, 249, 116834 DOI: 10.1016/j.carbpol.2020.116834
Brown et al, Chem. Eur. J. 2017. 23, 2315-2322, DOI: 10.1002/chem.201604832

7. Names of key academics and any collaborators:

Professor Steven P. Brown, University of Warwick
Professor Stephen J. Eichhorn, University of Bristol
Professor Rob Field, University of Manchester
Professor Yaroslav Z. Khimyak, University of East Anglia
Dr Frederic J. Warren, Quadram Institute Bioscience
Professor Philip T. F. Williamson, University of Southampton

8. Sources of significant sponsorship (if applicable):

EPSRC funding for the High-Field Solid-State Nuclear Magnetic Resonance Facility
EPSRC/Innovate UK funding (with Unilever and Croda)
BBSRC ISP for Quadram Institute Bioscience

9. Who should we contact for more information?

Professor Yaroslav Z Khimyak, School of Pharmacy, University of East Anglia y.khimyak@uea.ac.uk

1. Title of Case Study: Training activities at the UK High-Field Solid-State NMR National Research Facility
2. Grant Reference Number: EP/S035958/1, EP/S036458/1, EP/S036067/1
3. One sentence summary: Providing solid-state NMR spectroscopy awareness and training opportunities to liquid-state NMR spectroscopists at the UK High-Field Solid-State NMR National Research Facility.
One paragraph summary: The National Research Facility (NRF) has hosted two in-person NMR workshops (in 2022 and 2023) providing training activities covering the most important theoretical and practical aspects of solid-state NMR spectroscopy that were delivered by members of the NRF's Facility Executive. These workshops were successful as evidenced by several metrics including their oversubscription from members of the UK NMR community, the range of career stage from PhD student to Professor represented, ongoing new collaborative projects being discussed, and the positive feedback received from the delegates.
5. Key outputs in bullet points: • *Creating awareness of solid-state NMR spectroscopy methodologies and capabilities to solution-state NMR scientists using state-of-the-art high-field NMR instrumentation* • *Training in 2022 and 2023 of 30 early career researchers and established scientists from 19 UK academic institutions and 3 industries in solid-state NMR spectroscopy* • *New collaborations with the Universities of Bristol, Kingston, Oxford, and Imperial College London* • *Increasing visibility of the UK High-Field Solid-State NMR National Research Facility amongst other NMR heavy users*
6. Main body text: The NRF works with the Connect NMR UK network initiative to deliver training in solid-state NMR. The collective national vision for Connect NMR UK is to maximise the impact of the UK NMR infrastructure by connecting the NMR communities in the physical and life sciences together to support, enhance and extend their current efforts by creating synergies. One of the main objectives is to coordinate workshops and training opportunities in order for the UK NMR community to promote the NMR discipline and share their NMR expertise within the other subdisciplines of NMR and the wider fields such as organic chemistry and materials science. In this context, the NRF has hosted two Connect NMR UK "Solid-state NMR for liquid-state NMR scientists" workshops on Wednesday 30th March 2022 and Monday 27th March 2023. These events strategically took place on the days that preceded the 2022 and 2023 NRF Annual Symposia, so as to also provide opportunities, beyond the training provided by the workshops, to allow the participants to attend the Annual Symposia and hear about the most recent research activities enabled by access to the Facility. These workshops were in-person events with direct interaction with the hardware, so as to maximise the awareness of the available high-field solid-state NMR infrastructure. They were both oversubscribed (*e.g.*, the 2022 event was 200% oversubscribed) and limited to 15 participants to provide the participants with the most useful hands on experience. All attendees had excellent knowledge in solution-state NMR (that is their project largely focused on NMR rather than using it for e.g. synthetic chemistry), but none in solid-state NMR. Whilst in 2022, early-career researchers (PhD students and postdocs) and research technical professionals, from several Universities or various industrial sectors, made all the attendees of the inaugural event, in

2023, most participants were academic members of staff spanning all career stage (from Lecturer to Professor) as well as research technical professionals.

In both years, the 15 participants were split into 3 different groups of a manageable size of 5, rotating between 3 different activities. These were delivered by Facility Executive members, namely Prof John Griffin lecturing on anisotropic NMR interactions that distinguish solid-state NMR from solution-state NMR, Prof Frédéric Blanc exploring experimentally a number of concepts discussed in the lecture and showcasing standard solid-state NMR experiments at 850 MHz in 2022 and at 1 GHz in 2023, together with the support of the Facility Management Team with Dr. Dinu Iuga and Dr. Trent Franks demonstrating Magic Angle Spinning and Charlie Whitewood providing administrative support.

Social interactions such as dinner on the previous days and lunch and tea breaks during the days of the workshops also enabled the strengthening of existing interactions and triggering new collaborative projects. For example, delegates shared their research interests and the facility executive members discussed how high-field solid-state NMR spectroscopy could be utilised in their research, opening up new collaborative research projects.

Excellent feedback was received from attendees, e.g. "*Thank you, for a really wonderful opportunity to experience and learn about solid state NMR. I found it fascinating and great to network with people in similar fields to my own!*" and "*Again thank you for organising the solid-state workshop. It was really useful!*" and from PIs who supported attendance of group members, e.g. "*My PhD student was absolutely buzzing when he came back - he was really impressed. In fact his one problem was that he choose not to stay for the NRF presentations the next day and realised that was a big mistake cause he now knew enough that he felt confident sitting through solid-state NMR talks!*"

Building on the success of these workshops, a third workshop is planned to take place on Wednesday 17th April 2024, the day before the 2024 Annual Symposium.

7. Names of key academics and any collaborators:

Professor Frédéric Blanc, University of Liverpool
Professor John M. Griffin, Lancaster University

8. Sources of significant sponsorship (if applicable):

EPSRC, BBSRC and MRC funding for the Connect NMR UK network grant

9. Who should we contact for more information?

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