National Research Facility Annual Report Template

This annual report will be reviewed by the EPSRC National Research Facility High Level Group 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 2022/23:

- Reporting Period for this Annual Report: **1st September 2021 – 31st August 2022**
- Deadline for Annual Reports**: 20th February 2023**
- Assessment by Panel**: March 2023**
- Feedback to Facilities: **April 2023**

Please complete and return the Annual Report to researchinfrastructure@epsrc.ukri.org (and cc: kay.yeung@epsrc.ukri.org) by 20th February 2023.

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):

What is your facility uniquely placed to provide for UK research?

The current value proposition of this NRF is an evolution of the statement made last year since underlying Government policy, i.e., BEIS's roadmap document (7/20) and its more recent new Innovation Strategy (7/21) did not fundamentally change. However the major new context is the Autumn Statement 2021, which resulted in the updating of key UKRI and EPSRC strategy and policy documents throughout 2022. The most directly relevant are in order of cascade: the new UKRI strategy (3/22), and UKRI corporate plan (8/22) and EPSRC's delivery plan (9/22). Taking the cue from the overarching UKRI strategy, infrastructure features most prominently in Objective 2 (World-class places), specifically sub-objective 2.3, as well as 3.1. Infrastructure is woven throughout all three of these documents by the acknowledgement of the need to help enable the best research and to attract the best talent to the UK: there is the need for the UK to possess and operate effectively cutting-edge research infrastructure. This aim is manifest in this NRF as it currently offers two solid-state NMR instruments (850 MHz, 1 GHz) with associated state-of-the-art probe technology, which the Facility

Executive (FE) through its carefully planned investment plan has ensured remains cutting edge. The infrastructure supported by highly experienced research technical professionals in the facility management team.

Such an NRF plays directly into the objective to make coherent investment decisions for solid-state NMR by considering the need of the whole UK by the FE looking across the entire user community, optimising investments (within grant profiles) to maintain world-class infrastructure of highest relevance to the field. The value proposition is maximised by employing highly trained, expert personnel at a 'centre of excellence'. There is no doubt that the NRF has a strong profile and reputation world-wide for solid-state NMR, greatly enhancing the likelihood of the UK attracting the best scientists who need access to such capability. NRFs, in general, and certainly exemplified by this NRF, clearly play into the identified objective of EPSRC's delivery plan of ensuring the leading-edge nature of the infrastructure it funds. The value proposition is enhanced as it plays into the levelling up agenda by having an NRF located in the West Midlands. There is the additional advantage that the West Midlands is also one of the three regions that has been designated an innovation accelerator. The very broad range of research and innovation that uses solid-state NMR means that research carried out (see other sections) can map directly onto four of the seven EPSRC innovation priority areas. In the recently launched EPSRC delivery plan, the importance of discovery research is emphasised which NMR broadly contributes to, as well as to some of the mission-inspired priorities.

2) Scientific Excellence

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:

- Important scientific breakthroughs that have been supported by the facility;
- New methodologies that have been developed;
- Case studies that have been produced, with links if possible;

The High-field Solid-State NMR NRF provides users with access to high magnetic fields and specialist ancillary equipment, resulting in a widely-used facility with internationally leading infrastructure. The high magnetic fields provide substantial gains in sensitivity and resolution; opening up the study of challenging isotopes and complex materials. During the reporting period, these attributes have enabled the NRF to support scientific advances across a diverse range of research areas. We report here the first publications resulting from access from 2021 to the first 1 GHz (23.5 Tesla) NMR spectrometer in the UK.

The NRF has a long track record of supporting new research in inorganic materials science by opening up nuclei that are very challenging to observe at lower magnetic fields. Perrson and co-workers carried out a structural study of a set of novel titanium phosphate materials with potential applications in waste water treatment (*Dalton Trans.* 2022, 51, 8192-8207). The materials studied were weakly-ordered making them challenging to study by diffraction. The high magnetic field (850 MHz, 20 Tesla) enabled direct observation of $^{47/49}$Ti in the materials. These nuclei are notoriously difficult to observe owing to their low receptivities, often large quadrupolar interactions, and the fact resonances from both nuclei are usually observed simultaneously because of their very close resonance frequency which complicates spectral interpretation. However, the significant reduction in quadrupolar broadening at 20.0 T enabled distinct resonances from two chemical environments to be observed and parameterised. In addition to the structural insights into the studied materials, this work contributes significantly to the challenging field of $^{47/49}$Ti NMR, for which relatively few NMR parameters have been reported in the literature. In another study, Hanna and co-workers successfully obtained ^{39}K MAS NMR spectra at 20 T for a set of potassium-incorporated $Cs_2AgInCl_6$ double perovskite nanocrystals (*J. Mater. Chem. A* 2022, 10, 3562-3578). These materials have potential optoelectronic applications, but the band structure and photoluminescence properties are very sensitive to the local arrangements of cation dopants. The high sensitivity and chemical shift dispersion at 20 T enabled distinct cubooctahedral and octahedral K environments to be distinguished and quantified in the materials studied. This is a particularly impressive result as ^{39}K is a very low sensitivity nucleus and resonances were further broadened by structural disorder. This work opens the way for future studies of other perovskite systems via this nucleus. Fan *et al*. used ^{93}Nb static NMR at 20.0 T to probe the Nb environments in a Nb,Al-doped mesoporous silica catalyst (*Angew. Chem.* 2022, 61, e202212164). An extensively quadrupolar-broadened signal consistent with a tetra-coordinated environment was observed for the pristine catalyst, whereas a much narrower penta-coordinated resonance was observed after adsorption of a bio-derived reactant target molecule. Schroder, Yang & co-workers used ^{71}Ga NMR to probe the structure of a Ga-metal-organic framework (MOF) with photocatalytic properties for the reduction of CO_2 (*CCS Chem.* 2022, 4, 2560). ^{71}Ga is a highly sensitive nucleus, but suffers from extensive second-order quadrupolar broadening, making spectra challenging to acquire. At 20.0 T under fast MAS, it was possible not only to observe the one-dimensional ^{71}Ga NMR spectrum, but to record a two-dimensional ^{1}H-^{71}Ga dipolar correlation spectrum from which relative proximities between Ga sites and different ^{1}H environments in the structure. As well as providing insight into the MOF structure, this work opens the way for the study of other Ga-containing materials by advanced correlation experiments.

For applications to organic molecules, Harris and co-workers used high-field ^{13}C and ^{15}N solid-state NMR measurements to support the development of a new protocol for structure determination from powders (*Chem. Sci.* 2022, 13, 5277). Using a combination of powder X-ray and electron diffraction data, DFT calculations and high-field ^{13}C NMR data, it was possible to solve the structure of a new polymorph of *L*-tyrosine. Here, the high magnetic field (20 T) was necessary to fully resolve all ^{13}C resonances in the spectrum which were then correlated with DFT-calculated chemical shifts. Wilson and co-workers also combined diffraction data with high-field ^{1}H and ^{13}C solid-state NMR data to characterise the structure of the active pharmaceutical ingredient salbutamol oxalate (*Cryst. Growth Des.* 2022, 22, 4696-4707). The accurate measurement of ^{13}C and ^{1}H chemical shifts under high field (20 T) and very-fast MAS (60 kHz) conditions enabled discrimination of different molecular conformations by comparison with DFT calculations. These were monitored across a range of different crystallisation conditions to provide insight into the link between the local structure and the bulk processing properties. This study highlights how high-field NMR contributes to the development of advanced characterisation protocols that go beyond the long-range structural picture provided by traditional diffraction methods. Berge *et al*. demonstrated a new method for characterising CO_2 binding modes in a prototypical MOF for carbon capture and storage (*Nature Commun.* 2022, 13, 7763). The materials were dosed with ^{17}O-enriched CO_2, and it was possible to obtain high-quality ^{17}O MAS NMR spectra at 23.5 T (1 GHz) which clearly distinguished between carbamate and carbamic acid formation leading to a complete description of the adsorption mechanism.

Reflecting the partial funding of the NRF by BBSRC, work carried out at the NRF has continued to provide insights into the interplay of biopolymers in the structure of plant cells. Dupree and co-workers performed high-field ^{13}C solid-state NMR experiments at the Facility to study the structure and role of glucomannan, which is a hemicellulose found in plant cell walls (*Plant Cell*, 2022, 34, 4600-4622). In contrast to other hemicelluloses, glucomannan is poorly understood and neither its structure nor its functions within the plant cell wall have been fully resolved. The high-field NMR data (at both 850 MHz and 1 GHz) enabled observation and assignment of β-galactoglucomannan (β-GGM) extracted from eudicot plant cell walls. Here, the high magnetic field was crucial to enable resolution of the distinct sites in the crowded two-dimensional refocused INADEQUATE spectra. The similarity of the solid-state NMR ^{13}C chemical shifts to previously determined solution-state ^{13}C chemical shifts showed that there was no major conformational change in the cell wall. Through comparison of cross- and direct-polarisation 2D refocused INADEQUATE spectra, it was possible to determine that β-GMM is relatively immobile in the cell wall, as a consequence of its binding to cellulose, highlighting the necessity to consider the contribution of multiple hemicelluloses and their interactions in the functional study of plant cell walls.

As well as supporting structural research into material systems, the NRF has enabled new methodological research. Brown and co-workers used the Facility to optimise the performance of phase-modulated Lee-Goldburg (PMLG) homonuclear dipolar decoupling under fast-MAS conditions to enable through-bond ^{1}H-^{15}N correlation experiments (*Phys. Chem. Chem. Phys.* 2022, 24, 20258). Such experiments can provide significant structural insight into hydrogen-bonded systems, but remain very challenging to implement owing to the strong ^{1}H-^{1}H dipolar coupling interactions in most organic solids which reduce resolution and increase spin dephasing during through-bond correlation pulse sequences. This work showed that combining the high magnetic field (23.5 T) with very-fast MAS (60 kHz) and an optimised homonuclear decoupling sequence enabled the direct ^{1}H resolution to be maximised with baseline resolution between the CH_2 protons which was not possible at lower field. This 1 GHz result is also 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.

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.

The NRF makes all case studies (dating back to 2016) available on its webpage: https://warwick.ac.uk/fac/sci/physics/research/condensedmatt/nmr/850/case_studies/ For this annual review, we provide two new case studies describing the application of high-field solid-state NMR to fast ion conductors and for probing mechanisms in inorganic materials. These are appended at the end of this report (see #14).

3) Publications

Please list the publications for the last 3 years of operation of the current award (by year), Please highlight the top publications for the year.

Also identify any publications that have been prepared for a wider audience.

How do 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 this annual review, users were 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 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:

https://warwick.ac.uk/fac/sci/physics/research/condensedmatt/nmr/850/publications/

Concerning publications for a wider audience, the NRF was featured, including an interview with the Director, in a Chemistry World article in June 2022 to mark the announcement of the funding call for 1.2 GHz NMR (see #12): https://www.chemistryworld.com/news/boost-for-uk-xfel-hopes-as-ukri-unveils-research-infrastructure-plans/4015835.article

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. For the 2022 papers, we have endeavoured to respond to the feedback on 2021 report by sharing the panel feedback with the users when asked to prepare these sentences: *"Lots of publications listed but the panel would like a feel as to how critical the facility was to the publication."* That said we note that, for many papers, invaluable data recorded at the NRF is combined with complementary insight from other analytical science methods to give a full picture.

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 cntre 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$_2$AgInCl$_6$ 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$_2$AgInCl$_6$ 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.

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. *J. Phys. Chem. 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. *J. Phys. Chem. 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. *Magn. Reson. Chem. 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. *Magn. Reson. Chem. 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. *Magn. Reson.,* 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). *Cryst. Growth Des. 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. *Mol. Pharm. 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.

2020

Ashbrook, S. E., Dawson, D. M., Gan, Z., Hooper, J. E., Hung, I., MacFarlane, L. E., McKay, D., McLeod, L. K., & Walton, R. I. (2020). Application of NMR Crystallography to Highly Disordered Templated Materials: Extensive Local Structural Disorder in the Gallophosphate GaPO-34A. *Inorganic Chemistry*, *59*(16), 11616–11626. https://doi.org/10.1021/acs.inorgchem.0c01450

The multiple types and levels of disorder present in the material GaPO-34A can uniquely be probed using solid state NMR using ^{1}H, ^{13}C, ^{31}P, ^{19}F, and ^{71}Ga where the high field facility was used for ^{71}Ga satellite transition (STMAS) measurements.

Barney, E., Laorodphan, N., Mohd-Noor, F., Holland, D., Kemp, T., Iuga, D., & Dupree, R. (2020). Toward a Structural Model for the Aluminum Tellurite Glass System. *Journal of Physical Chemistry C, 124*(37), 20516–20529. https://doi.org/10.1021/acs.jpcc.0c04342

Neutron diffraction, thermal analysis, and ^{27}Al double-quantum MAS dipolar correlation NMR spectroscopy were performed on an Aluminium Tellurite glass leading to a charge balance model of the internal glass structure.

Cook, D. S., Hooper, J. E., Dawson, D. M., Fisher, J. M., Thompsett, D., Ashbrook, S. E., & Walton, R. I. (2020). Synthesis and Polymorphism of Mixed Aluminum-Gallium Oxides. *Inorganic Chemistry*, *6*, 3805-3816. https://doi.org/10.1021/acs.inorgchem.9b03459

Mixed Aluminum-Gallium oxides useful in electronics and catalysis are synthesized at low temperatures and characterized using ^{27}Al and ^{71}Ga solid state at the high field facility.

Griffiths, K., Halcovitch, N. R., & Griffin, J. M. (2020). Long-Term Solar Energy Storage under Ambient Conditions in a MOF-Based Solid−Solid Phase-Change Material. *Chemistry of Materials*, *32*, 9925-9936 DOI: 10.1021/acs.chemmater.0c02708

This study demonstrated a new mechanism for capturing and storing solar energy using photoresponsive molecules occluded within a metal-organic framework. Solid-state NMR was used to investigate the behaviour of the guest molecule, with high-field ^{1}H fast-MAS NMR supporting that it is highly dynamic when occluded within the MOF, thereby rationalising the efficient photoswitching that was observed.

Grüne, M., Luxenhofer, R., Iuga, D., Brown, S. P., & Pöppler, A. C. (2020). ^{14}N-^{1}H HMQC solid-state NMR as a powerful tool to study amorphous formulations-an exemplary study of paclitaxel loaded polymer micelles. *Journal of Materials Chemistry B*, *8*(31), 6827–6836. https://doi.org/10.1039/d0tb00614a

The quadrupolar coupling in ^{14}N-^{1}H HMQC experiments is shown to be helpful to resolve similar sites in amorphous samples where different magnetic fields shift the individual sites depending on their individual properties where the high field experiments were collected at the NRF.

House, R. A., Rees, G. J., Pérez-Osorio, M. A., Marie, J. J., Boivin, E., Robertson, A. W., Nag, A., Garcia-Fernandez, M., Zhou, K. J., & Bruce, P. G. (2020). First-cycle voltage hysteresis in Li-rich 3d cathodes associated with molecular O2 trapped in the bulk. *Nature Energy*, *5*(10), 777–785. https://doi.org/10.1038/s41560-020-00697-2

The voltage hysteresis of Li-rich cathode materials is explained by a loss of honeycomb structure and the formation of molecular O_2 as observed with a multi-technique analysis including ^{7}Li and ^{17}O NMR.

Kilpatrick, A. F. R., Rees, N. H., Turner, Z. R., Buffet, J. C., & O'Hare, D. (2020). Physicochemical surface-structure studies of highly active zirconocene polymerisation catalysts on solid polymethylaluminoxane activating supports. *Materials Chemistry Frontiers*, *4*(11), 3226–3233. https://doi.org/10.1039/d0qm00482k

The activation of zirconocene catalyst ornamentations on solid methylaluminoxane is characterized using polymerization experiments and ^{91}Zr NMR analysis consistent with surface Zr environments.

Koev, T. T., Muñoz-García, J. C., Iuga, D., Khimyak, Y. Z., & Warren, F. J. (2020). Structural heterogeneities in starch hydrogels. *Carbohydrate Polymers*, *249*(August), 116834. https://doi.org/10.1016/j.carbpol.2020.116834

Starch hydrogels, and the role of water in the formation of the gels, are characterized by multidimensional ^{1}H and ^{13}C solid state NMR that emphasize the static and dynamic portions of the samples.

Li, C., Pramana, S. S., Bayliss, R. D., Grey, C. P., Blanc, F., & Skinner, S. J. (2020). Evolution of Structure in the Incommensurate Modulated $LaNb_{1-x}W_xO_{4+x/2}$ (x = 0.04-0.16) Oxide Ion Conductors. *Chemistry of Materials*, *32*(6), 2292–2303. https://doi.org/10.1021/acs.chemmater.9b04255

The structural evolution between a modulated and unmodulated phase of an oxide ion conductor is revealed through high-field ^{17}O and ^{93}Nb spectra.

Mann, S. K., Pham, T. N., McQueen, L. L., Lewandowski, J. R., & Brown, S. P. (2020). Revealing Intermolecular Hydrogen Bonding Structure and Dynamics in a Deep Eutectic Pharmaceutical by Magic-Angle Spinning NMR Spectroscopy. *Molecular Pharmaceutics*, *17*, 622–631. DOI: 10.1021/acs.molpharmaceut.9b01075

Variable-temperature two-dimensional ^{1}H NOESY solid-state NMR spectra obtained at the NRF are key to distinguishing intermolecular from intramolecular contacts, showing the close association of ibuprofen and lidocaine in a deep eutectic pharmaceutical.

Page, S. J., Gallo, A., Brown, S. P., Lewandowski, J. R., Hanna, J. V., & Franks, W. T. (2020). Simultaneous MQMAS NMR Experiments for Two Half-Integer Quadrupolar Nuclei. *Journal of Magnetic Resonance*, *320*, 106831. https://doi.org/10.1016/j.jmr.2020.106831

Two MQMAS NMR experiments are simultaneously collected using a triply-tuned probe and multiple receivers.

Rees, G. J., Day, S. P., Barnsley, K. E., Iuga, D., Yates, J. R., Wallis, J. D., & Hanna, J. V. (2020). Measuring multiple ^{17}O-^{13}C: J-couplings in naphthalaldehydic acid: A combined solid state NMR and density functional theory approach. *Physical Chemistry Chemical Physics*, *22*(6), 3400–3413. https://doi.org/10.1039/c9cp03977e

Naphthaladehydic acid is characterized using multinuclear NMR with scalar coupling measurements to determine the multiple O functionalities of the lactone head group where high field data recorded at the NRF was needed for reducing quadrupolar linewidths and improving resolution in ^{17}O echo and MQMAS experiments.

Rice, C. M., Davis, Z. H., McKay, D., Bignami, G. P. M., Chitac, R. G., Dawson, D. M., Morris, R. E., & Ashbrook, S. E. (2020). Following the unusual breathing behaviour of ^{17}O-enriched mixed-metal (Al,Ga)-MIL-53 using NMR crystallography. *Physical Chemistry Chemical Physics*, *22*(26), 14514–14526. https://doi.org/10.1039/d0cp02731f

The structure, motion, pore size and shape, and composition of a terephthalate metal organic framework (MOF) is investigated by ^{17}O solid state NMR where the NRF provided a second field as required to fit the spectroscopic properties of the sample.

Rowlands, L. J., Marks, A., Sanderson, J. M., & Law, R. V. (2020). ^{17}O NMR spectroscopy as a tool to study hydrogen bonding of cholesterol in lipid bilayers. *Chemical Communications*. https://doi.org/10.1039/d0cc05466f

The hydrogen bonding environment of cholesterol in lipid bilayers is investigated using the solid state NMR provided by the high field facility and ^{17}O doped cholesterol.

Seymour, V. R., Griffin, J. M., Griffith, B. E., Page, S. J., Iuga, D., Hanna, J. V., & Smith, M. E. (2020). Improved Understanding of Atomic Ordering in $Y_4Si_xAl_{2-x}O_{9-x}N_x$ Materials Using a Combined Solid-State NMR and Computational Approach. *Journal of Physical Chemistry C*, 3–5. https://doi.org/10.1021/acs.jpcc.0c07281

The long range order indicated by neutron diffraction and the short-range disorder indicated by solid state NMR ^{15}N, ^{27}Al, and ^{29}Si spectra are reconciled, where the NRF was used to collect MQMAS ^{27}Al data for component analysis.

Vandeginste, V., Cowan, C., Gomes, R. L., Hassan, T., & Titman, J. (2020). Natural fluorapatite dissolution kinetics and Mn^{2+} and Cr^{3+} metal removal from sulfate fluids at 35 °C. *Journal of Hazardous Materials*. https://doi.org/10.1016/j.jhazmat.2020.122150

The kinetics of Mn^{2+}, Cr^{3+}, and acid removal from contaminated water using fluorapatite is monitored with ^{43}Ca NMR where Ca exchanges for the toxic heavy metals and can be is monitored through NMR.

4) Impact

Training, Outreach and Societal Impacts (max. 1 page): For the reporting period please provide evidence of the broader impact that the facility has through its outreach and training activities. This could include:

- Brief description of training courses and workshops held by the facility for its users / potential users and any benefits highlighted by the participants;
- Activities to promote the facility beyond its core user base;
- Facility staff training and career development;

- Public engagement;
- Examples of societal & economic impacts that the facility has created or been involved with.

In the aftermath of COVID-19 restrictions, the NRF's engagement with the userbase has transitioned back towards in-person activities, although retaining some of the benefits of hybrid interaction learnt during lockdown. The main engagement activity was the 2022 Annual Symposium which was held in March at the University of Warwick with optional hybrid attendance. The Symposium attracted 53 in-person attendees with a further 83 attending online. This represents a strong return to pre-pandemic in person attendance, and the additional online attendees mean that the Symposium now has a much wider reach. The hybrid format enabled the international participation of an invited speaker who would have been otherwise unable to attend. The symposium also featured an industrial speaker from the pharmaceutical industry, representing one of the key sectors that the NRF works with.

In conjunction with the Annual Symposium, the NRF hosted the first ConnectNMR UK NMR Solid-State NMR workshop on the preceding day in March 2022. The in-person event, which was 200% oversubscribed, was limited to 15 participants who rotated between 3 different activities of a manageable size of 5. This was delivered by FE members Dr John Griffin and Dr Frédéric Blanc together with the support of the FMT: John gave a lecture, Dinu & Trent demonstrated MAS, and Frédéric ran standard solid-state NMR experiments at 850 MHz. All attendees had good 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. 11 were PhD students, 2 postdocs, and 2 research technical professionals. 14 different universities were represented (there were 2 attendees from the University of Manchester, but coming from 2 different groups). 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 cos he now knew enough that he felt confident sitting through solid-state NMR talks!". Building on the success of this workshop, a second workshop will take place in March 2023.

Other engagement activities with the wider research community within the reporting period included the co-organisation of an online seminar entitled "Solid-State NMR for Materials Analysis" which was run in conjunction with Society of Chemical Industries (SCI) Materials Committee. This one-day event in October 2021 attracted 260 registrations from the UK and Europe with peak attendance at any one talk of 200. The seminar included a presentation about the capabilities and activities of the NRF and as a result of this and the interaction with the SCI, a new user from UCL from outside the NMR community has since submitted two proposals to the NRF for experimental time. Other outreach activities have also been undertaken by the FMT to broaden awareness of the Facility beyond existing users. To reach out to the medical research community, Dr Dinu Iuga gave talks on "@GHz NMR" at the International Society for Magnetic Resonance in Medicine (ISMRM) international conference in London (May 2022). Potential industry users were targeted by a talk entitled "The UK High Field SSNMR Facility: Access for Industry" also given by Dinu Iuga at the online meeting of UK solid-state NMR industry group (May 2022). To continue outreach to a wider userbase within and beyond the core NMR community, the NRF Twitter account has been regularly updated with user activities, user publications and retweeting of relevant NMR information. The NRF YouTube channel has also been maintained with an additional Research Snapshot video recently added and a further two in preparation by NRF users.

Throughout the reporting period, the NRF has continued to provide training to the userbase (see #6), in particular 22 PhD students and 10 PDRAs (with 4 and 2, respectively, being new users of the NRF), who gained valuable experience using the world-leading equipment. In addition, the Technical Director and Facility Manager travelled twice to the University of Birmingham in April/May 2022 to share their fast-MAS expertise in the testing of the compressed air supply for a new 0.7 mm probe which had been ordered by Birmingham.

The NRF has continued to support industrial research with 5 directly industry-funded PhD students and a further 4 with additional industry support. In addition to this, industrial use of the Facility was made by direct access, and one of the PDRA users was part-funded by industry. Industrial users continue to be represented at the highest level with Dr Stephen Day (Johnson Matthey) sitting on the Oversight Committee.

Facility staff have carried out a range of activities that have contributed to their own career development as well as publicising the NRF. In addition to the talks referred to above, Dr Trent Franks gave an invited on-line talk on “Solid-state NMR for Structural Biology: Applications and Overview” to the “Metals in Biology” BBSRC network. Dr Dinu Iuga attended the EUROMAR international NMR conference and presented a poster on “^{17}O High-Field Solid-State NMR for characterization of hydrogen bonding in pharmaceutical compounds”. Dr Iuga has also initiated a collaboration with Cryogenics Ltd focusing on the development of 3D printed probe and rotor components. This collaboration has involved a contribution to a Cryogenics presentation at the EUROMAR conference, and investment of Cryogenics investment in 3D printing equipment at the NRF. Both Dr Iuga and Dr Franks were co-applicants on the successful £17M 1.2 GHz EPSRC application (EP/X019640/1, see #12).

5) Cost Recovery

Please report on the sustainability returns for each year of operation of the current award, as an overall % recovery of running costs and also the actual figures. This includes headings of grant charges, other academic users, students, industry and Other charges for each year against the actual cost of running the facility. A narrative of future plans and issues is required below the table.

The NRF has two cost recovery income mechanisms:

(i) 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 using JeS, the agreed 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”) in the Research Council Facilities tab. In addition, the total cost must be added as a separate item under “Other Directly Incurred Costs” with the “Is Exception” boxed ticked on the JeS form, checking that funds are added to the total at 100% requested value. The procedure is described on the NRF website:

https://warwick.ac.uk/fac/sci/physics/research/condensedmatt/nmr/850/grant_applications_for_access/

(ii) 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)

We report in the below Table costs incurred in running the Facility (consumables and direct salary costs of the Facility Management Team and the Administrator) and income that was credited during the reporting period.

Year	Running Costs	Grants	Other Academic	Students	Industry	Other	% recovered cf costs
Sept 2021 to August 2022	£278,616	£12,637			£6,000		7%

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, the NRF is close to reaching this target in the reporting period.

During the reporting period, two grants with funded days at the NRF started or were announced: Dr David Xie (EP/V002236/2, 15 days) and Prof. Russell Morris (EP/W034824/1, 21 days). In addition, Dr Phil Williamson has also secured 3 days of institutional pump-prime funding. Also consider 10 days on a NERC grant to Thomas McDonald and Frédéric Blanc (NE/V010778/1 whose allocation at the NRF only started in July 2021 (i.e., after this reporting period). Taken altogether, 22 days have been used/ allocated from July 2022 to June 2023, i.e., corresponding to healthy continued grant income.

Concerning interaction with industry, as discussed below (see #6), there is a high number of PhD student users with industry support (9 out of 22), showing industry relevance of the NRF. The Facility Executive is striving to increase the number of days of paid-for industry access. For example, the NRF PIs and the NRF Facility Management Team actively participate in meetings of the UK solid-state NMR industry group that launched in 2022 (see #4). Moreover, at the suggestion of the industry member of the oversight committee, a survey was taken by the industry representative of why there is relatively little direct use of the NRF by UK industry. The results of this survey are being considered by the Facility Executive and will be reviewed at the next Oversight Committee meeting in March 2023.

6) Users

<u>Please report on Users by year of operation of current award. This needs to be broken down in category of user – student, academic, industry, other. We would like to know unique user numbers and repeat user figures. 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. How many of the users are new as a % of users this year?</u>

Note that the reported timeline here and in other below sections corresponds to the NRF's 6-monthly time-allocation periods:

Total combined for two cycles that most closely match the NRF reporting periods (July 2021 to June 2022, 850 MHz and 1 GHz)

July 2021 to June 2022	PhD Student		PDRA		Academic (PI[c])		Industry		Other	
Total unique users	22[a]		10[b]		31		1[d]		3[e]	
New users	4	18%	2	20%	7	23%	0	0%	0	0%

[a] Funded by EPSRC (7, including via the CDT in Molecular Analytical Science and the NNL and Green CDT, and 4 with additional industry support from Bruker, GlaxoSmithKline, Johnson Matthey and Pfizer), Faraday Institution (3), The Leverhulme Trust (1), ERC (1), Chinese Government Scholarship (1), University funding, including 2 via external donations (3), industry (5, AstraZeneca, Bruker, GSK, Johnson Matthey, and SG Chemicals). Visitors via the EU funded PANACEA project (1).

[b] Funded by EPSRC (1), Faraday Institution (3), BBSRC (2), MRC (2 including a UKRI Future Leaders Fellowship), ERC (2, with 1 with additional support from industry, Nyobolt)

[c] 26 applicants to the TAP process (see # 10 KPI table for University and Department information), 2 Fast-Track applicants, 2 test days with the Facility Management Team, 1 EU-funded PANACEA user

[d] Johnson Matthey

[e] Including University research staff and an overseas academic collaborator of a UK-based PI

The research split (by day of usage) is presented in this Table:

Research area split	Materials		Bio-molecular solids (including plant cell walls)		Methods		Pharmaceuticals and self-assembly	
	days	%	days	%	days	%	days	%
July to Dec 2021 (850 MHz)	97	61%	37	23%	3	2%	22	14%
July to Dec 2021 (1 GHz)	76	51%	55	37%	0	0%	18	12%
Jan to June 2022 (850 MHz)	113	79%	16	11%	1	1%	13	9%
Jan to June 2022 (1 GHz)	63	44%	45	32%	6	4%	29	20%
Combined	349	59%	153	26%	10	2%	82	14%

The above statistics reflect the importance of the NRF to a wide range of science applications (see also #2 and #3) across EPSRC also the BBSRC, MRC and NERC remits. In addition, the high number of PhD student users with industry support (9 out of 22) is noted: while the number of directly paid for industry days is low (see #5 and #8), this shows the high relevance of the facility to a industry sectors including pharmaceuticals and fine chemicals.

The NRF continues to place an emphasis on expanding the user base (see also #4). 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 time allocation panels: namely test days provided by the Facility Management Team after an email inquiry.

7) 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.

Average scores (July 2021 – June 2022, the NRF’s time allocation periods)
Rating : 1 Low / 5 High

PI feedback questionnaires (28 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 (62 sent, 28 responses received) - Requested every six months after every time allocation round.

Q1. Ease of arranging accommodation	4.9
Q2. Quality of accommodation	4.7
Q3. Location of accommodation	4.9
Q4. Support from FM upon arrival	4.9
Q5. Support throughout your visit	4.8
Q6. Quality of NMR facilities	4.6
Q7. Quality of the sample preparation area and storage facilities	4.5
Q8. Ease of access to the facility out of hours	5.0
Q9. Your overall time at the facility	4.8
Q10. Arrangements for accessing data	4.5
Q11. Arrangements for returning any samples	4.6
Q12. Reimbursement of expenses	4.3

The Facility Executive continued to use an additional questionnaire related to the changed way of facility access during the COVID-19 pandemic:
Remote visitor experience (62 sent, 19 responses)

Q1. Ease of sending samples to the Facility	4.9
Q2. Assistance from the Facility prior to start of experiments (e.g., advising on experimental set-up)	4.4
Q3. Ease of establishing remote access via Teamviewer (this question is about any IT or connectivity issues)	4.6
Q4. Assistance from the FMT during experiments (e.g., FMT inserting probes, inserting and spinning rotors, and tuning probes)	4.6
Q5. Experience of running experiments remotely via Teamviewer	4.6
Q6. Ease of receiving samples back from the Facility [If applicable at time of completing survey]	4.7

Q7. When in-person visits to the Facility are possible again, indicate your preference for in-person visit (5) compared to remote access (1).	4.1

The Facility Executive and the Oversight Committee review 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 to enhance the quality of the user experience. Visitor questionnaires are sent every six months: We noted the low response rates for the first six months and we were then more pro-active in sending reminders, so as to much improve the participation rate, for the second six months (see also KPI reporting, #10 below).

8) Service Demand

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

We report from July 2021 to June 2022 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 2021	1 GHz July to Dec 2021	850 MHz Jan to Jun 2022	1 GHz Jan to Jun 2022
Time Allocation Panel (TAP) allocated days	82% (150)	82% (151)	79% (143)	82% (149)
Fast Track	3% (5)	1% (1)	1% (1)	1% (1)
Industrial (Paid-for contract research)#			1% (2)	
PANACEA EU project			3% (5)	
Facility manager research & test days	6% (11)	5% (9)	10% (19)	7% (12)
Installation / calibration	4% (7)	1% (1)	3% (5)	3% (6)
Maintenance	4% (7)	5% (10)	3% (6)	3% (6)
Compensation	2% (4)	2% (3)		
Spectrometer not usable		4.9% (9)		4% (7)
Total	184	184	181	181

#Johnson Matthey

Considering panel feedback on the 2021 report: “Scheduled vs unscheduled downtime would have been an interesting data set to see.” We emphasise first that the Facility runs 24/7, 365 days a year. User research accounts for between 83 and 85% of the total time. The remainder of time is reserved for spectrometer issues, as and when they arise, and for facility manager research; indeed when the schedule is done for a 6-month period after each time allocation meeting, ~15% of days are left unallocated. Days devoted to spectrometer issues are separately reported as installation / calibration, maintenance, compensation (this is when a user could not do their planned experiments during a visit due to a technical issue, usually relating to the rf probe) and spectrometer not usable (for the new 1 GHz spectrometer it is regrettable that there were two major downtime incidents during the first year of usage, in the warranty period, see also #10). The maintenance days are responsive in the sense that they are taken when an issue arises during a user visit: the nature of solid-state NMR experiments is that these are mostly related to issues with the magic-angle spinning (MAS) probes, be they due to spinning issues at the fast rotation frequencies or rf performance issues. NRF operation as it is is only possible because of the high technical skill of the Facility Management Team in being able to complete such maintenance in house. We further note that the days nominally for facility manager research have to be taken flexibly to accommodate changes in the schedule caused by the quite frequent occurrence of a specific MAS probe not being available or when a user requests a change in their scheduled time, e.g., due to a sample not being ready, or difficulties with finding users for the Christmas to New Year times (this explains the higher number at 850 MHz, January to June 2022).

The below set of tables show an analysis for the TAP allocated days.

Service Demand (by day)	850 MHz July to Dec 2021		1 GHz July to Dec 2021		Total: 850 MHz & 1 GHz: July to Dec 2021	
Applicant type	*requested*	*Actual days scheduled and used*	*requested*	*Actual days scheduled and used*	*requested*	*Actual days scheduled and used*
Outside Warwick (Facility Executive)	19	12	16	18	35	30
Outside Warwick (not Facility Executive)	43 (+72[a])	95	30 (+72[a])	59	145	154
Warwick (Facility Executive)	4 (+6[a])	24	34 (+6[a])	37	44	61
Warwick (not Facility Executive)	15 (+8[a])	19	21 (+8[a])	37	44	56
number of access days requested	81 (+86[a])		101 (+86[a])		268	
number of access days scheduled	150		151		301	

Service Demand (by day)	850 MHz Jan to Jun 2022		1 GHz Jan to Jun 2022		Total: 850 MHz & 1 GHz: Jan to Jun 2022	
Applicant type	*requested*	*Actual days scheduled and used*	*requested*	*Actual days scheduled and used*	*requested*	*Actual days scheduled and used*
Outside Warwick (Facility Executive)	12 (+29[a])	34	22 (+29[a])	26	63	60
Outside Warwick (not Facility Executive)	60 (+36[a])	87	52 (+36[a])	47	148	134

Warwick (Facility Executive)	12	1	24	21	36	22
Warwick (not Facility Executive)	0 (+25[a])	21	39 (+25[a])	55	64	76
number of access days requested	84 (+90[a])		137 (+90[a])		311	
number of access days actually scheduled and used	143		149		292	

[a] denotes days where the user indicated no preference for the 850 MHz or 1 GHz spectrometer.

It is observed, for July to December 2021, that fewer days were requested than available – this is the first time that this happened since the start of Facility operation in 2010. This can be explained by the ongoing impact of the COVID pandemic continuing to place significant restrictions on user visits at that time. This situation was handled by the time allocation panel awarding one or two extra days for each of 28 individual projects submitted. In the following time allocation period, there was a return to more days requested than available, albeit by a smaller margin that in pre-COVID times.

Following the COVID-19 pandemic, the Facility has now (February 2023) largely returned to in-person operation although the NRF continues to offer remote access where required. This option was more popular in the first half of the reporting period when social distancing meant that the NRF had to restrict visits to one user per instrument and many institutions still had some level of travel restrictions. The availability of remote access helps to uphold the NRF’s commitment to EDI by facilitating access for those for whom an in-person visit to the NRF is harder to integrate with caring or family responsibilities, as well as reducing the NRF’s carbon footprint.

A further feature to note is that by far the highest number of days in each time period was for users who are neither from the host Institution or the five other Universities represented by the 8-person Facility Executive.

9) Risks

Is there a Risk Register for the facility? How is this used, give some examples of changes that have been made as a result.

The NRF notes the panel feedback on the 2021 report: “The risk register was viewed as ok, although it was a surprise that there wasn’t anything on lessons learnt from covid on remote working, training, and planning could benefit from this.” The Facility Executive has fully reviewed the below risk register, in particular adding to points 1.2 and 2.2 and creating new sections 3.2, 4 and 5 relating to helium supply shortages, remote operation and cost pressures. Review of the risk register will be a standing item at future six-monthly Facility Executive and annual oversight committee meetings.

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 facility management team secondment, in person or online, to assist with remote experiments during rebuilding and reequipping. 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 local management team 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. However, the historical turnover of staff since the start of Facility operation (2010) or instances of absence is extremely low.

2.1 Director

The management of the NRF through the Facility Executive mitigates the impact if the Director is unavailable. A Deputy Director, Dr Jeremy Titman, Nottingham, 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.

2.2 Facility Management Team (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 much 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 changed user expectation. Mitigation will be for the Facility Executive together with the Oversight Committee and the wider userbase, during the statement of need and NRF renewal process that is due to occur in 2023 and 202,4 to consider carefully the appropriate staffing levels, in particular by comparison to similar NRFs and STFC facilities such as the Diamond synchrotron that offer 24/7, 365 days a year operation.

2.3 Administrator

Current processes are understood across the local management team as well as across the wider Physics department administration team as a fail-safe.

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 (work to be undertaken in 2023). 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.

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.

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.

10) 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 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 panel.

QUERY LOG Jul 21 – Jun 22			
Respond to query within 5 working days: 99% and above, >90% < 99%; <90%			
Query Log KPI: A query log will be maintained by the NRF, split between active and completed queries. The log will include enquiries regarding the facility, advice for users, guidance to users etc. Respond to queries within 5 working days. Data reported every 6 months.			
		Replied within 5 working days	% Replied within 5 working days
Queries from users (email threads, time for response, not FE)	2334	2334	100%
Fast-track applications by existing users (time for acknowledgement)	4	4	100%
Fast-track applications by new users (time for acknowledgement)	2	2	100%
PhD travel fund applications (time for acknowledgement)	2	2	100%
conference publicity fund applications (time for acknowledgement)	0	N/A	

USAGE INFORMATION Jul 21 – Jun 22	Round 25 (Oct 31st 2021 deadline, 850 MHz & 1 GHz)	Round 26 (April 30th 2022 deadline, 850 MHz & 1 GHz)	Combined
number of access days requested	311	387	698
number of access days awarded	262+42 reserve	265 days + 42 reserve	527 days + 84 reserve
% of access requests responded to within 10 wds of TAP	100%	100%	100%
number of distinct PIs	18	18	26
number of distinct universities	9	10	12
Department type			
Chemistry	10	7	12
Physics	4	3	4
Engineering (including Chemical Engineering)	3	3	4
Biological or Life Sciences		2	2
Biochemistry	1	1	2
Materials		1	1
Pharmacy		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)	1 in Mechanical Engineering (not solid-state NMR expert)	

DOWNTIME								
Percentage downtime: <10%, >10% but < 20%, >20%	2021				2022			
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%	10	5%	6	3.3%	6	3.3%
user granted a compensation day	4	4%	3	2%	0		0	
Spectrometer Down	0	2%	9	5%	0		7	3.8%
Total	11	6%	22	12%	6	3.3%	13	7.1%
engineer installation days (not counted as downtime)	7		1		5		6	

FEEDBACK	July to Dec 21 (184 days)			Jan to June 22 (181 days)		
Complaints: The NRF will report the number of user complaints and response times. Data reported every 6 months.	No of Complaints	First response within 3 days	Full resp. within 10 working days	No of Complaints	First response within 3 days	Full resp. within 10 working days
95% and above; >90% but < 95%; <90%	0	N/A	N/A	1	yes	yes
USER SATISFACTION SCORES: 4; 3; 2	No:	Average score		No:	Average score	
Visitor Survey	27 Questionnaires Sent, 8	4.5		35 Questionnaires Sent, 20 received (Users)	4.8	

	received (Users)			
Remote user survey	27 Questionnaires Sent, 3 received (remote visitors)	5.0	35 Questionnaires Sent,22 received (remote visitors)	4.6
Annual PI Questionnaires	28 Questionnaires sent 22 received	4.7	Remote PI feedback (6)	4.7

DISSEMINATION EVENTS		
	July to Dec 21	Jan to June 22
Perform a minimum of one dissemination activity per year	Connect NMR workshop (in-person, 30th March 2022) and Annual Symposium (hybrid in-person & online, 31st March 2022)	
New snapshot videos hosted on YouTube	0	0
Number of followers of Twitter account	345	389
Information emails sent by the Facility to mailing list	2	1

PUBLICATIONS	
The NRF will report the numbers of publications acknowledging the Facility. Data reported annually.	
KPI Number of outputs 15; 12; 10	16 (2021)
RESEARCH OUTPUTS (TALKS & POSTERS)	
Number of Research Outputs, including talks, posters etc. Data reported annually.	
KPI Number of outputs 50; 30; 20	25* (2021)
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	9* (2021)
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	9 (2021)

Comment on the targets with ratings below green: Following the pattern established from the timing of previous annual reports that had a submission deadline before the end of the calendar year, data is reported for the COVID affected year of 2021. Given that very few in-person scientific meetings took place in 2021, user dissemination activities were much reduced explaining the red scores for RESEARCH OUTPUTS (TALKS & POSTERS) and OUTREACH TO A WIDER AUDIENCE. For the DOWNTIME, for the July to December 2021 time allocation period on the 1 GHz spectrometer, an amber score is reported: this is principally due to a fault that occurred, during the warranty period of the new Bruker system, that took a week to be fixed, with 9 days when the spectrometer was unusable. There was one complaint that related principally with issues associated with the University-managed accommodation that the NRF makes available to users. While some of the difficulties were related to COVID protection measures that the University accommodation had implemented, the NRF thoroughly reviewed the complaint and made changes to protocols in light of the issues that had arisen. The NRF has also reviewed its complaints procedure to ensure alignment with that of UKRI.

11) Links

<u>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?</u>

The capability and outputs of the NRF are at the cutting edge and are well-known internationally. Formally, the NRF's oversight committee (OC) provides an annual forum to review this and provide strategic guidance to the Facility Executive (FE). There are two eminent overseas solid-state NMR spectroscopists on the OC (for the reporting period: Prof. Mei Hong, MIT, USA, and Prof. Anne Lesage, Lyon, France), as well as a solid-state NMR spectroscopist from UK industry (Dr Stephen Day from Johnson Matthey) and a user representative, who is an early career researcher and user of the Facility (currently Dr Greg Rees, Oxford). Wider input is provided by three further members who represent another NRF, a CDT and the Diamond synchrotron, namely, Prof. Rik Brydson (SUPERSTEM), Prof. Stephen Skinner (Imperial, Materials Characterisation CDT) and Dr Julia Parker (beamline scientist at the Diamond Light Source), with Brydson the OC chair.

As noted in #4, outreach to the other research communities was initiated through communication with the Society of Chemical Industries Materials Committee and the Metals in Biology BBSRC Network. These interactions resulted a joint workshop on *Solid-State NMR for Materials Analysis* (October 2021) and the Facility Management Team member Trent Franks giving a seminar introducing the NRF (January 2022). The NRF also partnered with the EPSRC-funded ConnectNMR UK network (<u>https://www.connectnmruk.ac.uk/</u>) to offer a training workshop for scientists with solution-state NMR expertise, but no or very little solid-state NMR experience, the day before the NRF annual symposium in March 2022. This successful in-person event was attended by 11 PhD students, 2 postdocs, and 2 research technical professionals, and will be repeated in March 2023.

The NRF instrumentation at 850 MHz and 1 GHz are integrated into the PANACEA project, A Pan-European solid-state NMR Infrastructure for Chemistry-Enabling Access (https://panacea-nmr.eu/) , that started in September 2020 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: with the relaxation in COVID restrictions, the first PANACEA visitors came from Poland in June 2022.

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.

12) 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 and any proposed equipment upgrades 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. In the last year, significant investment has been made to enhance the capabilities of our existing 850 MHz and 1 GHz spectrometers, whilst funding has been secured not only for the continued development of these instruments, but also the expansion of the NRF to include a 1.2 GHz NMR spectrometer.

With the consortium of PIs that make up the Facility Executive of the NRF successfully securing UKRI funding (EP/X019640/1, £17M) for the 1.2 GHz spectrometer at the NRF, this will ensure that the UK research community retains access to the world's highest field commercially-available spectrometer. With delivery expected in early 2025, the spectrometer will mark a departure for the Facility as it will accommodate the needs of both the liquid- and solid-state NMR communities. Accordingly, the spectrometer will be equipped with a 3 mm TXI cryoprobe optimised for proton detection and $^{13}C/^{15}N$ decoupling in addition to a 5 mm TXO cryoprobe optimised for $^{13}C/^{15}N$ detection, both of which are well suited to biomolecular liquid-state NMR. To support the liquid-state users, a new research technical professional will be recruited to the facility management team who will be dedicated to the support of the liquid-state NMR community. Solid-state NMR users will benefit from a range of Bruker and Phoenix double, triple, and quadruple resonance NMR probes with MAS frequencies up to 111 kHz. Collectively the probes will offer a broad tuning range allowing the measurement of a diverse selection of NMR active nuclei ensuring the system offers an ideal platform for users from the material and life sciences communities.

Whilst securing funding for the investment in the 1.2 GHz spectrometer, the NRF has continued to support the diverse user base of the 850 MHz and 1 GHz spectrometers, investing in up-to-date MAS probes for both systems. New probes have been purchased to enhance the capability of the spectrometers whilst replacing/providing a degree of degeneracy for some of our older, but more heavily used probes. In the last year, in response to user requests, a 7 mm LASER high-temperature probe has been installed at 850 MHz allowing users to acquire NMR data at up to 1000 K. To complement this, the NRF has secured EPSRC Core Equipment Funding (EP/X03481X/1, £483k) that will equip the 850 MHz with a low temperature MAS probe and low-temperature MAS cabinet, with delivery and installation expected in 2023. Collectively, these probes will allow researchers to study materials and molecular processes across a range of temperatures from ~100 to 1000 K providing valuable insights into the structure and dynamics in materials and the molecular processes underpinning catalysis. The 850 MHz spectrometer has also benefited from the delivery of a Phoenix quadrupolar resonance HFXY 1.6 mm MAS probe that provides excellent low-temperature capability down to 170 K. The HFXY probe will not only provide redundancy for the ageing 2.5 mm HFX probe, thereby ensuring continued ^{19}F capabilities, but provide enhanced spinning frequencies (up to 45 kHz) and for the first time at the Facility the possibility of performing quadruple resonance experiments.

With the continued move to higher MAS frequencies and proton detected experiments the NRF have also invested in a 0.5 mm HCN MAS probe for the 1 GHz spectrometer which provides users with access to 150 kHz spinning speed. The increase in spinning frequency (from the 110 kHz currently available) provides enhanced proton resolution and sensitivity that has proved valuable when studying biomolecular systems in the solid state. To support users of the fast-MAS probes across all our spectrometers the NRF secured EPSRC Core Equipment Funding (EP/X03481X/1) for an ultra-centrifuge and packing tools. These will facilitate packing of the smaller rotors maximising the material packed into them whilst minimising sample dehydration that can negatively impact spectral resolution.

13) Website

Please include a link to your website. 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) 454 followers.

The main website is currently being used as both an information resource hub for new and established users as well as an administration tool for the LMT (Local Management Team). Since July 2020, operational improvements have been made to the web site including:

a. Continued improvements of users information collection for example, the visitor check-in process or the accommodation request booking process using webform tools.

b. Use of the webform data to implement a smoother booking experience for users and importantly has enabled the management of operational information and data to be provided to the Facility Executive, the Oversight Committee and the funding agencies as simple as possible.

c. Continued use of social media platforms (Twitter/YouTube) to reach a wide potential future audience to ultimately generate future requests for access from a broad spectrum of potential users both within the academic & industrial community, as well as to generate awareness within the student population and beyond.

Outreach Analytics

Website Hits (July 2021 – Dec 2021)

July - Dec 2021	Total Hits	On-Campus Hits	External Hits	Student Hits	Distinct IP addresses
July	747	21	726	1	650
Aug	831	28	802	5	738
Sept	836	29	806	4	702
Oct	1522	143	1376	32	1186
Nov	1139	64	1075	6	893
Dec	1086	24	1062	0	840

Website Hits (Jan 2022 – June 2022)

Jan - Jun 2022	Total Hits	On-Campus Hits	External Hits	Student Hits	Distinct IP addresses
Jan	1509	50	1459	4	1251
Feb	1409	47	1359	7	1201
Mar	2625	185	2430	7	1876
Apr	1937	64	1869	3	1420
May	1260	57	1203	15	1050
Jun	1014	41	973	4	798

Top Website Pages (July 2021 – Dec 2021)

Page name	Hits
National Research Facility	1234
Call for Applications	252
Publications	213
850 MHz Probes	186
1 GHz Probes	138
Applications for access	124
The Symposium 2021	96
Publicity	90
User Report	83
Fast track applications	75
NRF Pre-schedule check-in	74
Online application form	73
Information for Users	71
Project Visitor Declaration	65
Expense Claim	61

UK Solid-State NMR	59
Report a presentation	53
Reporting	51
Project Visitor Declaration	44
Contact	38
PhD theses	34
Service Level Agreement	33
Funding	29
Dinu Iuga CV	27
Acknowledgement	26
Grant applications for access	24

Top Website Pages (Jan 2022 – Jun 2022)

Page name	**Hits**
National Research Facility	1710
The Symposium 2022	1313
Annual symposia	448
Publications	308
Call for Applications	271
850 MHz Probes	234
1 GHz Probes	205
People (Local Management Team)	140
Travel fund	126
Contact	107
Applications for access	103
PhD theses	103
User Report	100
Online application form	97
NRF Pre-schedule check-in	96
Dinu Iuga CV	88
Expense Claim	86
Publicity	81
Fast track applications	79
The Symposium 2021	74

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)	subscribers	impressions
Total	360	4.6	13	637
Snapshot Video 1	96	1	1	91
Snapshot Video 2	37	0.7	1	52
Snapshot Video 3	37	0.3	0	96
Snapshot Video 4	43	0.4	0	89
Snapshot Video 5	42	0.3	0	136
Snapshot Video 6	98	1.8	1	173
Views per impression shown measures how often viewers watched a video after seeing an impression				

The UK High-Field Solid-State NMR Facility (@NrfHf) / Twitter (454 followers)

35 tweets in total 2021	July	Aug	Sept	Oct	Nov	Dec
Tweet impressions	1526	1174	1799	746	805	417
Profile visits	339	80	458	255	237	116
Mentions	1	6	1	3	6	6
New followers	9	7	9	3	7	6

43 tweets in total 2022	Jan	Feb	Mar	Apr	May	Jun
Tweet impressions	513	793	994	430	292	474
Profile visits	563	731	778	539	265	1,030
Mentions			8	13		8
New followers	7	10	7	10	4	4

14) Case Studies

Please include up to 3 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.

1. Title of Case Study: Solid-State NMR of Fast Ion Conductors

2. Grant Reference Number: EP/N004884/1, EP/M009521/1, EP/K031511/1, EP/H000925/1, EP/L015277/1, EP/S023259/1, Faraday Challenge Project SOLBAT, EU ERC LIBNMR

3. One sentence summary: Understanding of ionic transport in advanced functional materials is enabled by multinuclear ^{1}H, ^{6}Li, ^{7}Li, ^{17}O, ^{23}Na, ^{27}Al, ^{33}S and multidimensional NMR spectra obtained at the UK High-Field Solid-State NMR National Research Facility.

4. One paragraph summary: Solid-state NMR spectroscopy is a powerful tool for the atomic scale structural understanding of functional materials, yet can also be very effectively employed for the direct assessment, in a non-destructive manner, of site-selective ion dynamics and diffusion processes over a very wide range of timescales and temperatures. This case study illustrates the use of experimental solid-state NMR approaches to probe the mobility of Li^+ and O^{2-} ions specifically via ^{6}Li, ^{7}Li and ^{17}O that complement other approaches (for example, impedance). Many of the targeted nuclei (^{6}Li, ^{7}Li, ^{17}O, ^{23}Na, ^{27}Al, ^{33}S, ^{71}Ga, ^{93}Nb) are quadrupolar, some with poor receptivity, and their spectra benefit greatly from the enhanced resolution and sensitivity achieved at UK High-Field Solid-State NMR National Research Facility. Additionally, structural disorder induced by, for example, vacancies and interstitials play an important role in enabling this mobility and solid-state NMR spectra provide important information about the local structure. The identification of factors limiting ionic mobility coupled to the effects of structural modification provide a framework for the further development of advanced functional materials with enhanced ion transport for the next generation of energy storage and conversion technologies.

5. Key outputs in bullet points:

- *Understanding of ionic transport and disorder in advanced functional materials*
- *Key insights into developing new materials with enhanced properties*
- *Training of several early career researchers from multiple UK institutions in state-of-the NMR instrumentation*
- *New collaboration in NMR crystallography for the study of electrochemical devices*
- *Increasing visibility of the UK High-Field Solid-State NMR National Research Facility in flagship research (Faraday Institution, EU ERC) and training (CDT) programmes*

6. Main body text: In a series of three highly collaborative research papers, published in *Chem. Mater.*, that target the discovery of new Li^+ ion solid electrolytes of various compositions (Li_3AlS_3 and $Li_{4.3}AlS_{3.3}Cl_{0.7}$) for the future of all solid-state batteries, ^{27}Al Magic Angle Spinning (MAS) NMR spectra at a magnetic field strength of 20 Tesla, enabled the structural understanding of key Al_2S_6 dimer units consisting of Al tetrahedra. Upon sulphide S^{2-}/ chloride Cl^- anion mixing forming $Li_{4.3}AlS_{3.3}Cl_{0.7}$, a large degree of cationic site disorder on the Al tetrahedra is created, as revealed by high resolution multi-quantum MAS (MQMAS) NMR spectra, thatis associated with disordered Li^+ vacancies. This results in faster Li^+ mobility and the creation of three-dimensional diffusion pathways which are directly captured by ^{6}Li and ^{7}Li NMR. Sulphides are thus important ions and the ^{33}S nucleus offers an exciting avenue to understand its structure in energy materials. However, ^{33}S suffers from very poor receptivity arising from low gyromagnetic ratio, very low natural abundance and large quadrupolar moment, but its detection was successfully overcome in the Li^+ ion battery conversion electrode NbS_3 by combining high field at 20 Tesla too with large sample volume (almost 1 g) and advanced data acquisition strategies which was reported in *Chem. Comm.* The ^{33}S NMR data revealed spectral signatures for both S^{2-} and disulphide units S_2^{2-}, opening up avenues to provide local insights into the anionic redox behaviours during electrochemical cycling. The formation of a solid-electrolyte interface, which challenges the reversible operation of Li^+ ion batteries, often occurs during these redox processes. An NMR crystallography approach, published in *Nature Chemistry*, that deployed multinuclear ^{1}H and ^{7}Li MAS NMR at 20 Tesla jointly with first principles calculations contributed to the understanding of the decomposition products. The work notably revealed that the identity of the major organic solid-electrolyte interface on graphite anodes to be lithium ethylene mono-carbonate, rather than lithium ethylene di-carbonate as previously thought, paving the way for further understanding of electrochemical processes. A further NMR crystallography publication in *Magn. Reson. Chem.* this time employing ^{23}Na (MQ)MAS NMR at the highest field of 23.5 T of the Facility, established the local-range structure of a different type of anode material, namely conjugated alkali metal di-carboxylates which have received significant attention.

While these outcomes largely focused on Li^+ batteries, the last few years also saw interests in solid oxide fuel cell materials, in particular, those exhibiting fast O_2^- transport from the presence of oxygen interstitials for which discoveries were published in two papers in *Chem. Mater* that focus on materials with different compositions ($LaNb_{1-x}W_xO_{4+2/x}$ with $x < 0.17$ and $La_3Ga_{5-y}Ge_{1+y}O_{14+y/2}$, $y < 1.51$). The key here is the possibility for Ga^{3+} and Nb^{5+} cations to change their coordination numbers to accommodate extra oxygens which could be captured from ^{71}Ga and ^{93}Nb NMR spectral features such as the shift and quadrupolar parameters, thanks to known relationships between those and coordination numbers. The high external magnetic field of 20 T enabled highly resolved ^{71}Ga and ^{93}Nb (MQ)MAS NMR spectra to be collected and which were assigned to niobium and gallium tetrahedra extending their coordination to five in $LaNb_{1-x}W_{0.16}O_{4.08}$ and $La_3Ga_{3.5}Ge_{2.5}O_{14.75}$, respectively – that is hosting extra oxygens. These oxygen interstitials were then also detected directly in ^{17}O MAS NMR spectra on ^{17}O-enriched materials and allow for probing oxide ion diffusion pathways.

References: B. B. Duff *et al. Chem. Mater.*, **2023**, *35*, 27. J. Gamon *et al. Chem. Mater.*, **2021**, *33*, 8733 & **2019**, *31*, 9699. D. M. Halat *et al. Chem.Commun.*, **2019**, *55*, 12687. L. Wang *et al. Nature Chemistry*, **2019**, *11*, 789. T. Whewell *et al.*, *Magn Reson. Chem.*, **2022**, *60*, 489. M. Diaz-Lopez *et al. Chem. Mater.*, **2019**, *31*, 7183. C. Li *et al. Chem. Mater.*, **2020**, *32*, 2292.

7. Names of key academics and any collaborators:

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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?

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1. Title of Case Study: Applications of Solid-state NMR Spectroscopy for the Study of Mechanisms in Inorganic Materials

2. Grant Reference Number: EPSRC EP/L504749/1, MR/T043024/1, EP/S022953/1, EP/M022501/1, EP/S023755/1; 2017 ERC-COG MISOTOP project

3. One sentence summary: High-field solid-state NMR enables a wide range of mechanistic processes in inorganic materials to be understood using a wider range of nuclei than is typically accessible at lower magnetic fields.

4. One paragraph summary: The high sensitivity of NMR to the local chemical environment makes it a powerful probe of mechanistic processes where short-range interactions and structural properties can be very important, but are difficult to probe by diffraction-based structure determination methods. For inorganic materials, the wide range of nuclei present can offer opportunities to probe mechanistic processes from different perspectives to the more commonly studied nuclei such as ^{1}H, ^{13}C, ^{15}N in organic materials, potentially increasing the amount of information that can be obtained. However, this can simultaneously present challenges in the observation and interpretation of experimental data due to e.g., low natural abundance, low gyromagnetic ratio, large quadrupolar interactions, or a combination of these. This case study illustrates how high-field NMR offers significant advantages in the observation of challenging nuclei and/or complex processes to enable a wide range of phenomena to be characterised.

5. Key outputs in bullet points:

- *Atomic-level mechanistic insight into a range of systems of technological and industrial insight*
- *Training of early career researchers from multiple UK institutions in state-of-the NMR instrumentation*
- *Demonstration of solid-state NMR spectroscopy for low receptivity nuclei*
- *Publications in leading international journals*

6. Main body text

Metal-organic frameworks (MOFs) represent a diverse class of porous materials that are widely used and studied across chemistry and materials science. Despite this, many mechanistic aspects of their formation and function are difficult to characterise. One such question is that of the initial crystallisation process which remains poorly understood. Jones *et al*. used high-field *in situ* NMR to characterise the crystallisation mechanism of the model MOF MFM-500(Ni). The so-called “CLASSIC” NMR technique was used, where alternate liquid and solid-state NMR spectra are acquired as a solution begins to crystallise. ^{1}H NMR spectra revealed changes in the local environments of the organic linker groups as aggregration started to occur. Here, the high magnetic field was critical to allow resolution of liquid-like sharp components and broader components associated with aggregation of the linker. Using variable-temperature measurements, it was possible to extract activation energies for both nucleation and initial growth of the MOF crystallites. Crucially, this information is not possible to obtain by other methods such as diffraction which is only sensitive to long-range ordering which occurs after the initial aggregation. In another study, Berge *et al*. used ^{17}O NMR to probe the adsorption mechanism of ^{17}O-enriched CO_2 in a prototypical MOF for CO_2 capture and storage.^{17}O MAS NMR measurements at 23.5 T revealed distinct oxygen environments that could be assigned to carbamate formation within the amine group upon CO_2 adsorption. For this study, it was important to perform experiments at the highest possible magnetic field to minimise the large ^{17}O quadrupolar broadening to allow accurate fitting and deconvolution of the experimental data. By screening experimental data for a set of 22 amine-functionalised MOFs against calculated NMR parameters, it was possible to confidently distinguish carbamate and carbamic acid species and provide evidence for a mixed acid-carbamate adsorption mechanism.

The sensitivity advantages of high-field NMR make it possible to study nuclei with large quadrupolar interactions that are difficult to observe at low magnetic field. Dawson *et al*. used high-field ^{71}Ga MAS NMR to characterise an unusual low-temperature dehydrofluorination process in a gallium-phosphate zeolitic framework. The ^{71}Ga nucleus is very informative but has a very large quadrupole moment making it very challenging to observe. By combining high magnetic field (20.0 T) with fast MAS (60 kHz), it was possible to observe both four- and five-coordinate Ga sites which could be linked to environments in a DFT model for the dehydrofluorinated structure. Fan *et al*. used static ^{93}Nb NMR at 20.0 T to probe the Nb environments in a Nb,Al-doped mesoporous silica catalyst. A very broad signal consistent with a tetra-coordinated environment was observed for the pristine catalyst, whereas a much narrower penta-coordinated resonance was observed after adsorption of a bio-derived reactant target molecule.

Mechanistic processes have also been studied in non-porous solids via nuclei which hold significant structural information but which are challenging to observe. Chen *et al*. used ^{17}O MAS NMR at 20.0 T to probe the ^{17}O enrichment process of silica surfaces via the cost-effective approach of grinding with $H_2{}^{17}O$. The high-field enabled observation of weak SiOH surface group resonances resulting from the enrichment process which could not be seen at lower field without DNP enhancement. Kilpatrick *et al*. used static ^{91}Zr NMR to study catalytic zirconene complexes developed for olefin polymerisation. Using frequency-stepped experiments combined with CPMG for signal enhancement, it was possible to obtain full lineshapes for four zirconenes studied, opening up new possibilities for the future study of this important class of materials.

Jones *et al*., *Chem. Sci.* 2021, 12, 1486. Berge *et al*., *Nature Commun*. 2022, 13, 7763. Dawson *et al*., *J. Phys. Chem. C* 2021, 125, 2537. Fan *et al*., *Angew. Chem.* 2022, 61, e202212164. Chen *et al*., *Chem.- Eur. J.* 2021, 27, 12574. Kilpatrick *et al.*, *Mater. Chem. Frontiers* 2020, 4, 3226.

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