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 2020:

- Reporting Period for this Annual Report: **1st September 2019 – 31st August 2020**
- Deadline for Annual Reports**: 12st January 2021**
- Assessment by Panel**: February/March 2021**
- Feedback to Facilities: **March/April 2021**

NRF ANNUAL REPORT

Facility Name: **The UK High-Field Solid-State NMR Facility**
Director: **Professor Steven P. Brown (University of Warwick)**
Start/End Dates
Note that the reporting period covers the previous Funding Period (NS/A000061/1), 5th January 2015 to 4th January 2024, and the Current Funding Period (EP/T015063/1), 5th January 2020 to 4th January 2025
Funds awarded £2.7M (NS/A000061/1) and £2.4M (EP/T015063/1, to lead institution)

1) **Value Proposition (max ½ page):**

<mark>What is your facility uniquely placed to provide for UK research?</mark>
The NRF provides a cutting-edge high-field solid-state NMR facility for the UK physical sciences and life sciences community in both academia and industry. The 850 MHz wide-bore solid-state NMR system (4 channel HFXY spectrometer with 14 MAS (0.7 to 7 mm), DOR and static probes), is sited in the Magnetic Resonance Laboratory at Millburn House, University of Warwick. In 2020, a 1 GHz standard-bore (4 channel HFXY spectrometer with 7 MAS (0.7 to 7 mm) probes) system was added to the NRF as the UK's first 1 GHz NMR magnet at field, ensuring that the NRF remains internationally competitive. The NRF is managed by a Facility Executive (FE) that is composed of the Director (Steven Brown, Warwick), the Deputy Director (Jeremy Titman, Nottingham), the Technical Director (Dinu Iuga) and six members of the UK NMR community (Sharon Ashbrook, St Andrew's; Frédéric Blanc, Liverpool; John Griffin, Lancaster; Józef Lewandowski, Warwick; Mark Smith, Southampton; Philip Williamson, Southampton) whose expertise spans the field of technology development and applications in the physical and life sciences reflecting the diversity in the Facility's user community.

The value proposition of the NRF in the UK landscape can be understood in relation to key policy and strategy documents of EPSRC, UKRI and the Government (i.e., UKRI's Delivery Plan and its more detailed infrastructure roadmap (to 2030), EPSRC's Delivery Plan (6/19) and the recently published UKRI's Delivery Plan (10/20), which included recognition of the role UKRI plays in realising the ambition set out in the Government's overarching Research and Development roadmap (7/20)). Key to the Government's vision is to *'…put the UK at the forefront of attracting, retaining and developing diverse, talented people and the teams that will be critical to delivering the Government's science superpower vision.*' The document recognises several key factors for which there is substantial evidence that the Solid-State NMR NRF directly plays into. For example, it explicitly identifies that higher quality infrastructure will help attract and retain the best staff and create a more vibrant research environment. There is an indirect acknowledgement that to maximise wider support for researchers requires *'…including technical and infrastructure…*as well as… *internationally competitive, high-quality and accessible facilities…*'. It is recognised that world-leading infrastructure is a national asset, acting as a magnet for international talent. The outputs (see #2 and #3) show that the NRF contributes to the UK's performance in identified priorities of the productive (3.1.1) and healthy (3.1.3) nation in EPSRC's Delivery Plan. The NRF also continues to play into all of the three overarching, high level objectives of EPSRC's Delivery Plan, and into its aim to maximise efficiency through leading-edge infrastructure investments. Hence from the quality of the science underpinned, to the efficiency of the utilisation of a major infrastructure investment, to directly relating to central elements of the Government's, UKRI's and EPSRC's visions in the research space, the NRF offers a strong value proposition.

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 offers its users access to high magnetic field, as well as specialist equipment, including ultrafast magic angle spinning (MAS) and double rotation (DOR) probes which combine into an internationally-leading offer. The instrumentation available provides substantial gains as compared to lower magnetic field in both sensitivity and resolution, allowing NMR experiments on challenging isotopes with low receptivity or large quadrupolar couplings. The NRF supports a broad range of excellent science in the UK, from the development of novel NMR methods to atomic-level characterization of new materials. This section details outputs from papers with publication dates in the reporting window, i.e., from 1st September 2019 to 31st August 2020 (see full citations in #3). Note that case studies are discussed in #14.

Materials research at the NRF aims to characterize disordered, heterogeneous or defect structures, with technological applications that include as ionic conductors, electrodes, catalysts, adsorbents and refractory materials. This often involves measurements of quadrupolar nuclei with large quadrupole couplings which would not be feasible at lower magnetic fields. For example, Li *et al.* carried out ^{93}Nb NMR studies of the high temperature phase evolution of oxide ion conducting LaNb$_{1-x}$W$_x$O$_{4+x/2}$ materials to reveal a sequence of transformations between a modulated monoclinic phase, a modulated tetragonal phase and an unmodulated tetragonal phase. Their findings correlate with ion transport in these phases and offer insights into the design of new materials for solid-state electrochemical devices. Other research in the area of novel energy materials includes studies of voltage hysteresis in Li-rich cathodes which are potential candidates for next-generation lithium-ion batteries. Similarly, Gamon *et al.* used a probe structure search to discover a new sulfide phase, Li$_3$AlS$_3$ with similar lithium ion mobility to Li$_5$AlS$_4$. They applied synchrotron X-ray and neutron diffraction along with ^{6}Li and ^{27}Al MAS NMR to demonstrate that the phase has a new structural type with a highly ordered cationic polyhedral network within a sulfide anion *hcp* sublattice. AC impedance measurements revealed a low lithium mobility, strongly impacted by the presence of ordered vacancies.

Several studies made use of ^{71}Ga NMR with ultrafast MAS at rates up to 75 kHz. For example, Ashbrook *et al.* carried out a NMR crystallography investigation of a gallophosphate with an unusual framework composition and either 1-methylimidazolium or pyridinium as the structure-directing agent. They were able to show using X-ray crystallography, solid-state NMR and DFT calculations that the structure simultaneously contains occupational, compositional and dynamic disorder, preventing the growth of large single crystals for conventional structure determination. Similarly, Cook *et al.* studied polymorphism in mixed aluminium-gallium oxides, using a combination of ^{27}Al and ^{71}Ga MAS NMR to elucidate preferences in the occupancy of tetrahedral and octahedral sites. The combination of ^{17}O NMR and DFT calculations proved invaluable in studies of lability in zeolites and molecular dynamics in metal–organic frameworks. For example, Heard *et al.* showed that covalent bonds in chabazite are labile when in contact with neutral liquid water, leading to partial but fully reversible hydrolysis without framework degradation, while Rice *et al.*[9] characterized the unusual breathing behaviour of mixed metal (Al,Ga)-MIL-53 which cannot be described as the compositionally weighted average of the breathing behaviour seen for the Al and Ga end members.

Seymour and Smith used a similar combination of ^{29}Si and variable magnetic field ^{27}Al NMR with DFT calculations to develop new structural models for silicon aluminium oxynitrides. In environmental science Vandeginste *et al.* employed ^{43}Ca NMR to support studies of natural fluorapatite as a passive remediation material for mining-induced contamination of soils and groundwater in arid regions. In this study these researchers took advantage of apparatus for measuring low-receptivity isotopes available at the NRF.

DFT calculations can be extended to computations of couplings between nuclei, and a combined multi-nuclear NMR and DFT approach was used to determine the four heteronuclear $^1J(^{13}C,^{17}O)$ couplings in solid ^{17}O-enriched naphthalaldehydic acid by Rees *et al.* Solid-state NMR is a powerful method for studying the intermolecular interactions which drive crystallization, as well as the resulting phenomena of polymorphism. Al Rahal *et al.* prepared a new polymorph of L-tryptophan by crystallization from the gas phase, with structure determination carried out directly from powder XRD data augmented by DFT calculations. These researchers recorded a high-resolution ^{13}C NMR spectrum at the NRF taking advantage of the high magnetic field available. This was compared with the results of calculations and showed that there were two molecules of L-Tryptophan in the asymmetric unit. Understanding complex biological structures requires detailed information about the molecular assembly of the component

materials. Multi-dimensional ^{13}C NMR spectra recorded at the high magnetic field available at the NRF were used by Terrett *et al.* to analyse the polymer interactions in never-dried cell walls of the softwood, spruce. The results contrasted with earlier softwood cell wall models and resulted in a new model of softwood molecular architecture which explains the origin of the different cellulose environments. The new model will assist strategies for improving wood usage in a sustainable bioeconomy. A similar approach was used by Muñoz-García *et al.* to characterize the structure of bacterial cellulose hydrogels, to monitor local mobility and water interactions and to unravel the effect of composites with different glucans on the short-range order, mobility, and hydration of bacterial cellulose fibres.

In other work, Grüne *et al.* used ^{1}H-^{14}N correlation experiments to investigate amorphous-drug polymer formulations. Halat *et al.* reported ultra-wideline, natural abundance solid-state ^{33}S NMR spectra of the Li-ion battery conversion electrode NbS_3, the first ^{33}S NMR study of a compound containing disulfide units. The large quadrupolar coupling parameters are consistent with values obtained from DFT calculations, and the spectra provide evidence for a linear Peierls distortion that doubles the number of ^{33}S sites.

3) Publications

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. 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. As detailed in #4, in 2020, we have started to produce Snapshot videos (made available online) to make the key results from publications presenting NRF data more widely available.

2018

Bignami, G. P. M., Davis, Z. H., Dawson, D. M., Morris, S. A., Russell, S. E., McKay, D., Parke, R. E., Iuga, D., Morris, R. E., & Ashbrook, S. E. (2018). Cost-effective ^{17}O enrichment and NMR spectroscopy of mixed-metal terephthalate metal-organic frameworks. *Chemical Science*, *9*(4), 850–859. https://doi.org/10.1039/c7sc04649a

(H) The spectral resolution of the NRF instrument allowed for structural characterization by ^{17}O Double Rotation (DOR) Experiments and MQMAS NMR of Metal Organic Frameworks (MOFs) where the stoichiometry of the metals results in different porosity and fingerprint regions.

Bonhomme, C., Wang, X., Hung, I., Gan, Z., Gervais, C., Sassoye, C., Rimsza, J., Du, J., Smith, M. E., Hanna, J. V., Sarda, S., Gras, P., Combes, C., & Laurencin, D. (2018). Pushing the limits of sensitivity and resolution for natural abundance ^{43}Ca NMR using ultra-high magnetic field (35.2 T). *Chemical Communications*, *54*(69), 9591–9594. https://doi.org/10.1039/c8cc05193c

(M) Natural abundance ^{43}Ca NMR is explored with an experimental series-connected-hybrid 35.2 T magnet, where the NRF instrument at 20.0 T is used as a traditional high-field comparison.

Brown, S. P. (2018). Advanced solid-state NMR methods for characterising structure and self-assembly in supramolecular chemistry, polymers and hydrogels. *Current Opinion in Colloid and Interface Science*, *33*, 86–98. https://doi.org/10.1016/j.cocis.2018.02.005

(H) A review of available multidimensional solid state NMR methods correlating ^{1}H, ^{13}C, ^{11}B, and ^{15}N in various ways to investigate atomic-level structural differences in organic molecules, where several of the spectra were collected at the NRF.

Brown, S. P. (2018). Chapter 2: High-resolution ^{1}H 2D Magic-angle Spinning Techniques for Organic Solids. In *New Developments in NMR*, Royal Society of Chemistry (ed. Hodgkinson, P) https://doi.org/10.1039/9781788010467-00039

(H) A review of the state of the art of high-resolution ^{1}H direct and indirectly detected experiments for small molecules, where examples of typical ^{1}H-^{1}H, ^{1}H-^{13}C, and ^{14}N-^{1}H are taken from data collected at the NRF.

Fernandes, A., Moran, R. F., Sneddon, S., Dawson, D. M., McKay, D., Bignami, G. P. M., Blanc, F., Whittle, K. R., & Ashbrook, S. E. (2018). ^{17}O solid-state NMR spectroscopy of $A_2B_2O_7$ oxides: Quantitative isotopic enrichment and spectral acquisition? *RSC Advances*, 8(13), 7089–7101. https://doi.org/10.1039/c8ra00596f

(H) Quantitative ^{17}O labelling is demonstrated for perovskites with higher ^{17}O exchange temperatures than typical: the NRF was used to verify assignments and to quantify spectral properties such as the second order quadrupolar-dipolar cross terms for ^{17}O species.

Hooper, T. J. N., Partridge, T. A., Rees, G. J., Keeble, D. S., Powell, N. A., Smith, M. E., Mikheenko, I. P., Macaskie, L. E., Bishop, P. T., & Hanna, J. V. (2018). Direct solid state NMR observation of the ^{105}Pd nucleus in inorganic compounds and palladium metal systems. *Physical Chemistry Chemical Physics*, 20(41), 26734–26743. https://doi.org/10.1039/c8cp02594k

(H) The first direct ^{105}Pd solid state NMR measurements are reported on diamagnetic and metallic Pd, where the facility instrument was needed to determine the isotropic chemical shift and the quadrupolar product.

Hughes, C. E., Williams, P. A., Kariuki, B. M., & Harris, K. D. M. (2018). Establishing the Transitory Existence of Amorphous Phases in Crystallization Pathways by the CLASSIC NMR Technique. *ChemPhysChem*, 19(24), 3341–3345. https://doi.org/10.1002/cphc.201800976

(H) An amorphous phase is observed during the crystallization of a small organic molecule as monitored by interleaved solid-state and liquid state NMR ^{13}C experiments, where the high field facility provided spectral resolution for overlapped sites.

Kunicki, H., Chamberlain, T. W., Clarkson, G. J., Kashtiban, R. J., Hooper, J. E., Dawson, D. M., Ashbrook, S. E., & Walton, R. I. (2018). An expanded MIL-53-type coordination polymer with a reactive pendant ligand. *CrystEngComm*, 20(31), 4355–4358. https://doi.org/10.1039/c8ce00891d

(H) A method to introduce a Bromine atom into a metal organic framework (MOF) for later chemical modification is presented, where ^{81}Br spectra taken at the NRF reveal the possibility of C-Br bonds, and exclude the formation of $MgBr_2$, a breakdown product.

Neniškis, A., Račkauskaitė, D., Shi, Q., Robertson, A. J., Marsh, A., Ulčinas, A., Valiokas, R., Brown, S. P., Wärnmark, K., & Orentas, E. (2018). A Tautoleptic Approach to Chiral Hydrogen-Bonded Supramolecular Tubular Polymers with Large Cavity. *Chemistry - A European Journal*, 24(53), 14028–14033. https://doi.org/10.1002/chem.201803701

(H) The self-assembly of tubular nanoscale systems is shown to proceed through hydrogen bonding, where the NRF is used to map ^{1}H contacts in the hydrogen bonding network.

Ruengkajorn, K., Wright, C. M. R., Rees, N. H., Buffet, J. C., & O'Hare, D. (2018). Aqueous immiscible layered double hydroxides-AIM-LDHs. *Materials Chemistry Frontiers*, 2(12), 2277–2285. https://doi.org/10.1039/c8qm00407b

(H) Layered Double Hydrides are treated with an organic solvent where the organic molecules interact hydroxyl framework, where the NRF was able to provide the high magnetic field and fast-MAS probes needed to resolve the different hydrogen bonded protons in the sample using direct ^{1}H detection.

Seymour, Valerie R., Day, S. P., Scholz, G., Scheurell, K., Iuga, D., Griffin, J. M., Kemnitz, E., Hanna, J. V., & Smith, M. E. (2018). A Combined ^{25}Mg Solid-State NMR and Ab Initio DFT Approach to Probe the Local Structural Differences in Magnesium Acetate Phases $Mg(CH_3COO)_2nH_2O$ (n=0, 1, 4). *ChemPhysChem*, 19(14), 1722–1732. https://doi.org/10.1002/cphc.201800317

(H) The utility to investigate multiple molecular environments using ^{25}Mg NMR in several materials which is explored and compared to simulations using the NRF for unlabelled samples, and 2D Satellite Transition (STMAS) experiments to confirm the contribution of the assigned components.

Sternberg, U., Witter, R., Kuprov, I., Lamley, J. M., Oss, A., Lewandowski, J. R., & Samoson, A. (2018). ^{1}H line width dependence on MAS speed in solid state NMR – Comparison of experiment and simulation. *Journal of Magnetic Resonance*, 291(5), 32–39. https://doi.org/10.1016/j.jmr.2018.04.003

(H) The utility and limitations of ~100 kHz MAS rotation using ^{1}H detection is demonstrated on a biologically relevant small peptide comparing simulations with data obtained with instrumentation only available at the NRF.

Varghese, S., Halling, P. J., Häussinger, D., & Wimperis, S. (2018). Two-dimensional ^{1}H and ^{1}H-detected NMR study of a heterogeneous biocatalyst using fast MAS at high magnetic fields. *Solid State Nuclear Magnetic Resonance*,

92(February), 7–11. https://doi.org/10.1016/j.ssnmr.2018.03.003

(H) The molecular mechanism of the surface immobilization of a protein catalyst is investigated by Solid State NMR using cutting edge techniques for ^{1}H detection available only through use of the NRF.

2019

Al Rahal, O., Hughes, C. E., Williams, P. A., Logsdail, A. J., Diskin-Posner, Y., & Harris, K. D. M. (2019). Polymorphism of L-Tryptophan. *Angewandte Chemie*, *131*(52), 18964–18968. https://doi.org/10.1002/ange.201908247

(M) A new crystal polymorph of L-Trp is created by sublimation in the gas phase, where small differences in ^{13}C chemical shift are revealed by high-field solid state NMR.

Concistré, M., Kuprov, I., Haies, I. M., Williamson, P. T., & Carravetta, M. (2019). [14]N overtone NMR under MAS: Signal enhancement using cross-polarization methods. *Journal of Magnetic Resonance*, *298*, 1–5. https://doi.org/10.1016/j.jmr.2018.10.017

(M) The Overtone Transition (OT) can be used to produce narrow spectral lines in an [14]N-^{1}H correlation spectrum but is not sensitive, so Cross Polarization (CP) is used to excite this transition: experiments recorded at the NRF complement those recorded at lower magnetic field.

Dawson, D. M., Moran, R. F., Sneddon, S., & Ashbrook, S. E. (2019). Is the ^{31}P chemical shift anisotropy of aluminophosphates a useful parameter for NMR crystallography? *Magnetic Resonance in Chemistry*, *57*(5), 176–190. https://doi.org/10.1002/mrc.4788

(H) The use of [31]P Chemical Shift Anisotropy (CSA) is explored as a structural constraint, where the high field Facility is used for comparison with lower field because the magnitude of the CSA is greater at larger field.

Diaz-Lopez, M., Shin, J. F., Li, M., Dyer, M. S., Pitcher, M. J., Claridge, J. B., Blanc, F., & Rosseinsky, M. J. (2019). Interstitial Oxide Ion Conductivity in the Langasite Structure: Carrier Trapping by Formation of $(Ga,Ge)_2O_8$ Units in $La_3Ga_{5-x}Ge_{1+x}O_{14+x/2}$ ($0 < x \leq 1.5$). *Chemistry of Materials*, *31*(15), 5742–5758. https://doi.org/10.1021/acs.chemmater.9b01734

(H) Langasite is explored as a possible lower temperature solid oxide fuel cell, where [17]O, [71]Ga, and [73]Ga spectra acquired at the NRF point to carrier trapping in this material.

Gamon, J., Duff, B. B., Dyer, M. S., Collins, C., Daniels, L. M., Surta, T. W., Sharp, P. M., Gaultois, M. W., Blanc, F., Claridge, J. B., & Rosseinsky, M. J. (2019). Computationally Guided Discovery of the Sulfide Li_3AlS_3 in the Li-Al-S Phase Field: Structure and Lithium Conductivity. *Chemistry of Materials*, *31*(23), 9699–9714. https://doi.org/10.1021/acs.chemmater.9b03230

(H) A new sulfide Li_3AlS_3 is discovered by a combined computational-experimental method to find a new lithium solid electrolyte, where [6]Li and ^{27}Al NMR data collected at the NRF are combined X-ray and neutron diffraction.

Halat, D. M., Britto, S., Griffith, K. J., Jónsson, E., & Grey, C. P. (2019). Natural abundance solid-state [33]S NMR study of NbS_3: Applications for battery conversion electrodes. *Chemical Communications*, *55*(84), 12687–12690. https://doi.org/10.1039/c9cc06059f

(H) Wide-line natural abundance [33]S spectra collected at the NRF are presented using a frequency stepping approach including the first spectrum of a disulfide.

Heard, C. J., Ashbrook, S. E., Grajciar, L., Rice, C. M., Pugh, S. M., Nachtigall, P., & Morris, R. E. (2019). Fast room temperature lability of aluminosilicate zeolites. *Nature Communications*, *10*(10), 4690. http://dx.doi.org/10.1038/s41467-019-12752-y

(H/ M) Zeolites exchange framework oxygens with water at room temperature in under 24 hours but the framework is not broken as shown by [17]O, [27]Al, and [29]Si spectra, where the NRF was used to clearly resolve two similar Si-O-Al species.

Hughes, C. E., Walkley, B., Gardner, L. J., Walling, S. A., Bernal, S. A., Iuga, D., Provis, J. L., & Harris, K. D. M. (2019). Exploiting in-situ solid-state NMR spectroscopy to probe the early stages of hydration of calcium aluminate cement. *Solid State Nuclear Magnetic Resonance*, *99*(10), 1–6. https://doi.org/10.1016/j.ssnmr.2019.01.003

(H) Solid and soluble aluminum components are monitored by ^{27}Al NMR during the hydration of calcium aluminate cement at different temperatures, where all data was collected at the NRF.

Ihli, J., Clark, J. N., Kanwal, N., Kim, Y. Y., Holden, M. A., Harder, R. J., Tang, C. C., Ashbrook, S. E., Robinson, I. K., & Meldrum, F. C. (2019). Visualization of the effect of additives on the nanostructures of individual bio-inspired calcite crystals. *Chemical Science*, *10*(4), 1176–1185. https://doi.org/10.1039/c8sc03733g

(H) The mechanisms for controlling crystallization processes using soluble additives is explored in calcite crystals, where the NRF is used to confirm Mg substitution in calcite.

Jarvis, J. A., Concistre, M., Haies, I. M., Bounds, R. W., Kuprov, I., Carravetta, M., & Williamson, P. T. F. (2019). Quantitative analysis of ^{14}N quadrupolar coupling using ^{1}H detected ^{14}N solid-state NMR. *Physical Chemistry Chemical Physics*, *21*(11), 5941–5949. https://doi.org/10.1039/c8cp06276e

(H) An efficient ^{14}N-^{1}H correlation experiment is presented that allows the determination of the quadrupolar coupling interactions, where the NRF was used to prove the method for a challenging system.

Kanwal, N., Colaux, H., Dawson, D. M., Nishiyama, Y., & Ashbrook, S. E. (2019). Sensitivity improvement in 5QMAS NMR experiments using FAM-N pulses. *Solid State Nuclear Magnetic Resonance*, *100*, 1–10. https://doi.org/10.1016/j.ssnmr.2019.03.002

(H /M) A more efficient 5QMAS excitation and reconversion scheme is presented and subsequently implemented at the NRF (for ^{45}Sc), where the scheme is shown to greatly improve sensitivity.

Muñoz-García, J. C., Corbin, K. R., Hussain, H., Gabrielli, V., Koev, T., Iuga, D., Round, A. N., Mikkelsen, D., Gunning, P. A., Warren, F. J., & Khimyak, Y. Z. (2019). High Molecular Weight Mixed-Linkage Glucan as a Mechanical and Hydration Modulator of Bacterial Cellulose: Characterization by Advanced NMR Spectroscopy. *Biomacromolecules*, *20*(11), 4180–4190. https://doi.org/10.1021/acs.biomac.9b01070

(H) The long range order of bacterial cellulose hydrogels are found to be affected by the presence of arabinoxylan and xyloglucan, where the core, surface-bound, and surface domains are identified by NMR experiments performed at the NRF.

Öster, C., Kosol, S., & Lewandowski, J. R. (2019). Quantifying Microsecond Exchange in Large Protein Complexes with Accelerated Relaxation Dispersion Experiments in the Solid State. *Scientific Reports*, *9*(1), 1–11. https://doi.org/10.1038/s41598-019-47507-8

(H) Relaxation dispersion experiments in proteins are accelerated using paramagnetic doping to overcome low sensitivity, where the resolution in the fingerprint ^{1}H-^{15}N spectrum is improved by the NRF instrumentation.

Seymour, V. R., & Smith, M. E. (2019). Distinguishing between Structural Models of β'-Sialons Using a Combined Solid-State NMR, Powder XRD, and Computational Approach. *Journal of Physical Chemistry A*, *123*(45), 9729–9736. https://doi.org/10.1021/acs.jpca.9b06729

(H) One of four models of the replacement of silicon and nitrogen by aluminum and oxygen in β'-Sialons is found to be consistent with high field ^{29}Si and ^{27}Al NMR data collected at the NRF.

Terrett, O. M., Lyczakowski, J. J., Yu, L., Iuga, D., Franks, W. T., Brown, S. P., Dupree, R., & Dupree, P. (2019). Molecular architecture of softwood revealed by solid-state NMR. *Nature Communications*, *10*(1), 1–11. https://doi.org/10.1038/s41467-019-12979-9

(H) The polymer interactions between cellulose, xylan, and galactoglucomannan suggest a model of the softwood molecular architecture where the NRF was necessary to unambiguously differentiate between 2-fold, and 3-fold xylan using ^{13}C correlation experiments.

Wang, L., Menakath, A., Han, F., Wang, Y., Zavalij, P. Y., Gaskell, K. J., Borodin, O., Iuga, D., Brown, S. P., Wang, C., Xu, K., & Eichhorn, B. W. (2019). Identifying the components of the solid–electrolyte interphase in Li-ion batteries. *Nature Chemistry*, *11*(9), 789–796. https://doi.org/10.1038/s41557-019-0304-z

(H/ M) The solid-electrolyte interphase responsible for the reusability of lithium ion batteries is shown to be lithium ethylene mono-carbonate by a multi-technique approach including ^{1}H and ^{7}Li spectra collected at the NRF.

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

(M) 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

(M/H) 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

(H) 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.

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. (2020). Chemoenzymatic synthesis of fluorinated cellodextrins identifies a new allomorph for cellulose-like materials. *Chemistry – A European Journal*. https://doi.org/10.1002/chem.202003604

(H) 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.

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

(H) 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

(H) 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

(H) 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

(H) 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

(H) 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.

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

(M) 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

(H) 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

(H) 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

(H) 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

(H) 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

(H) 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.

With the renewal and expansion of the NRF under the current funding (see #12), the FE has developed a new communication and engagement strategy to proactively grow and diversify the user base. Part of this strategy focuses on close interaction with the RCUK-funded (EP/S035958/1) Connect NMR UK network which is co-led by Blanc, who joined the FE during the reporting period. Connect NMR UK aims to maximise the impact of UK NMR infrastructure through networking and training and the presence of Blanc on the FE will ensure that the capabilities of the NRF are effectively promoted to the wider UK NMR community. In addition to widening participation with other NMR-focused users, another key aspect of the NRF's strategy is to reach out to potential users outside of the NMR community. Indeed, "outreach to a wider userbase" has been included as a new key performance indicator since renewal of the NRF in January 2020 (see #10). To this end, links (see also #11) have already been made with the Faraday Institution (FI) which represents a large group of potential users. In May 2020, FE member Griffin presented an overview of solid-

state NMR for battery materials analysis as part of the Faraday "Masterclass" series, reaching an audience of over 140 FI members. This was followed up by a four-part online training series on solid-state NMR for FI post-docs and PhD students which was developed and delivered by FE members Griffin and Blanc. The NRF is also committed to increasing its visibility and accessibility to new users. As part of this, a significant redesign of the NRF website has been planned (as detailed in #13), with some changes already made within the reporting period. Notably, the NRF has established a Twitter feed and Youtube channel to reach out to an even wider audience. These platforms have been used to host short "Research SnapShot" videos produced by NRF users which showcase the research taking place.

The NRF has continued to provide training to the userbase (see #6), in particular 22 PhD students and 9 PDRAs (9 and 3 first-time visitors) who gained valuable experience using the world-leading equipment. In this context, note that Blanc and Griffin both used the 850 MHz instrument as a PDRA before taking up academic positions, with Griffin being the first user of the Facility in February 2010.

Throughout the reporting period, the NRF has continued to promote engagement with industrial users in order to enhance its impact outside the academic sector. In recognition of the role the NRF plays in industrial research, the tenth annual symposium was organised on the theme of "Industrial Applications of High-Field Solid-State NMR". The programme for the symposium featured four industrial speakers as well as five academics and students showcasing industrially-funded or industrially-relevant research. Unfortunately, the symposium could not go ahead as it coincided (March 2020) with the covid-19 outbreak; however, the speakers will be invited to give presentations at future symposia.

Industrial users continue to be represented at the highest level within the NRF. For the beginning of the reporting period, Stephen Byard from Arcinova was chair of the Oversight Committee (OC). As his tenure ended at the end of 2019, Dr Nathan Barrow from Johnson Matthey was appointed as an OC member in order to ensure the continuation of industrial representation.

In the current reporting period, the NRF hosted 6 industrially-funded PhD students. These projects involve companies across a range of sectors, namely AstraZeneca, Bruker, Johnson Matthey, Novozymes, and SASOL.

Concerning staff development, during the reporting period, the Facility Manager (and Technical Director under the new NRF funding) Iuga undertook online training courses in computer-aided design and 3D printing which are enabling him to push forward his own work on the development of home-built NMR capability (see #12) to increase the effectiveness of use of the NRF's state-of-the-art spectrometers.

5) Cost Recovery

Reporting period	Salary Costs	Running Costs	income from RCUK grants	income from industry contract research	% recovery
2020 (year 1 of current award, up to 31st August)	£90,037	£63,977	£23,965	£2,000	15

Under the previous funding award (5 years up to 4th January 2020), the NRF transitioned to partial cost recovery (80%) in years 4 and 5 (i.e., 2018 and 2019) from RCUK grants, with a per day rate that includes salary and running costs. The income reported above (as received by the Facility in the reporting period) is for two EPSRC and two BBSRC grants (PIs at Cambridge, Southampton and Warwick) funded during the previous funding award. In the current funding period, there is tapering of direct support from 80% to 75% to 70% to 65% to 60% in years 1, 2, 3, 4 and 5, respectively. There is a new SLA for grant applications for access: as stated in #10, 11 applications were received in the reporting period (green target of 10). A NERC grant providing access has recently been awarded to FE member, Blanc (Liverpool).

In this and following sections, data is reported from 1st July 2019 to 31st August 2020. The start date of 1st July 2019 (as opposed to the formal reporting period start date of 1st September 2019) corresponds to the NRF's six-month time allocation panel (TAP) cycle: note that all users (including PIs at the host institution and FE members) request days at the NRF, with allocation being made by a 3-person TAP. During the time allocation period 1st January to 30th June 2020, it was necessary to suspend all operations on March 21st 2020 due to the COVID-19 epidemic, and there was no spectrometer time usage from March 22nd to May 22nd 2020 (61 days: note that these days are excluded from the analysis in the below Tables). After May 22nd 2020, the NRF was able to provide a partial service if applicants were able send samples that could be run remotely (30 of the TAP allocated days were used in this way). All PIs who had used the spectrometer in the last 3 years were contacted and offered batches of up to 5 days of time if samples could be run remotely. PIs from Cambridge, Cardiff, Oxford, Sheffield, Southampton and Warwick took up this possibility and this ensured that the spectrometer was then used every day following restart of operations.

Type of user

July 2019 to Aug 2020	PhD Student	PDRA	Academic (PI)	Industry	Other
Total unique users	22[a]	12[b]	29	1	8[c]
new users	9 (41%)	3 (25%)	5[d] (17%)	0 (0%)	0 (0%)

[a] Funded by EPSRC (including a CDT in Molecular Analytical Science), BBSRC, ERC and Gatsby Charitable Foundation. 6 industrially-funded PhD students on projects involve companies across a range of sectors, namely AstraZeneca, Bruker, Johnson Matthey, Novozymes, and SASOL

[b] Funded by EPSRC, BBSRC, Innovate UK (with AstraZeneca and Infineum), Leverhulme Trust, MRC and Alzheimer's Research UK

[c] 5 research staff and 3 overseas visitors (collaborating with a UK PI)

[d] 2 with MR experience (though not solid-state NMR): James Garnett, Centre for Host-Microbiome Interactions, King's College London; Mick Mantle, Chemical Engineering and Biotechnology, Cambridge. 3 with limited or no previous solid-state NMR expertise: Peter Bruce, Materials, Oxford, energy materials; James Carter, Chemistry, Cardiff, catalysis; Jason Lynham, Chemistry, York, organometallics.

Research area split (by day of usage, as specified by the PI when applying for time and reporting their usage)

July 2019 to Aug 2020	Materials	Bio molecular Solids (including plant cell walls)	Methods	Pharmaceuticals and self-assembly
Research area split	51%	32%	9%	8%

Future Plans & Issues

As detailed in #12, new capability and a doubling of capacity has been achieved by the delivery and successful installation in autumn 2020 of a 1 GHz solid-state NMR system (the first 1 GHz NMR magnet at field in the UK): this will be available to users in early 2021. This will allow more PhD students and PDRAs to use the state-of-the-art systems. The proactive steps that the NRF is taking in the new funding period to increase and diversify the userbase are detailed in #4 and #13.

The NRF continues to take a proactive approach given limitations imposed by the ongoing COVID-19 pandemic. The time allocation process resumed for January 2021 to June 2021 (proposals submitted by October 2020 and reviewed by the 3-person time allocation panel in November 2020): the process was modified to request that users indicate if they can submit samples for remote analysis, and users were informed that if they cannot take up their allocated time (i.e., if they require in-person attendance and this is subsequently not possible) time will not be carried over.

7) User Surveys/Satisfaction

Average scores (Sept 2019 – Aug 2020)
Rating : 1 Low / 5 High

PI feedback questionnaires (33 sent, 28 responses received: requested once per year)

Q1. The ease of the application process	4.9
Q2. The transparency of the allocation procedure	4.8
Q3. The feedback on time requests	4.6
Q4. The scheduling of your time by the facility	4.7
Q5. Quality of results obtained at the facility	4.6

Visitors feedback questionnaires (27 sent, 21 responses received)

Q1. Ease of arranging accommodation	4.6
Q2. Quality of accommodation	4.5
Q3. Location of accommodation	4.7
Q4. Support from FM upon arrival	4.9
Q5. Support throughout your visit	4.8
Q6. Quality of NMR facilities	4.8
Q7. Quality of the sample preparation area and storage facilities	4.8
Q8. Ease of access to the facility out of hours	4.9
Q9. Your overall time at the facility	5.0
Q10. Arrangements for accessing data	4.9
Q11. Arrangements for returning any samples	4.9
Q12. Reimbursement of expenses	4.4

The Facility Executive and the Oversight Committee review questionnaire feedback at their six-monthly and annual meetings, including also specific comments entered into free text boxes. We continue to be pleased with the very high feedback scores received. The FE is currently reviewing the suitability of the survey questions where samples are being run remotely for a user due to COVID restrictions.

8) Service Demand

Noting also that spectrometers run 24/7, 365 days a year, there is over demand in the UK for access to high-field solid-state NMR, with all calls (since the start of Facility operation) oversubscribed, and further noting community behaviour reducing allocation requests to match the available instrument times (and there is maximum number of days (28) that an individual PI can request in each 6-monthly time-allocation period).

In the time allocation periods, as allocated for July 2019 to June 2020: 447 days were requested by PIs from 12 different institutions (Cambridge, Cardiff, Durham, Imperial College London, King's College London, Lancaster, Liverpool, Oxford, Sheffield, Southampton, St Andrews, STFC, University of East Anglia, Warwick), with 277 days TAP allocated. There was also one fast-track applications (3 days to a new PI from York and 14 days were allocated to UKRI (EPSRC and BBSRC) funded projects (PIs at Cambridge, Southampton and Warwick).

Applicant type	Requested (days)		Applicant type	Allocated (days)
Outside Warwick (Facility Executive)	**70**		Outside Warwick (Facility Executive)	**59**
Outside Warwick (not Facility Executive)	**221**		Outside Warwick (not Facility Executive)	**141**
Warwick (Facility Executive)	**50**		Warwick (Facility Executive)	**23**
Warwick (not Facility Executive)	**106**		Warwick (not Facility Executive)	**54**
Total	447		Total	277

Spectrometer time usage (1st July 2019 to 31st August 2020, excluding March 22nd to May 22nd 2020, 61 days, shutdown, see #6)

TAP allocated days	67.3%
COVID arrangements allocation (see #6)	18.5%
Facility manager research	5.7%
UKRI grant funded days	3.8%
Maintenance	1.9%
Compensation	1.4%
Fast track	0.8%
Industrial (Paid-for contract research)#	0.6%

The stated usage corresponds to contract research for Infineum. In addition, in the current reporting period, the NRF hosted 6 industrially-funded PhD students. These projects involve companies across a range of sectors, namely AstraZeneca, Bruker, Johnson Matthey, Novozymes, and SASOL.

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.==

Risk mitigation has been inherent to the previous and current applications for NRF funding – this is summarised below. #6 describes how the NRF has adapted to COVID restrictions on user access.

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.
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): some mitigation of risk associated with helium shortages is provided by recovery of helium gas boil-off by means of a helium liquefier in the Department of Physics at the University of Warwick.

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, Jeremy Titman, Nottingham, is in place along with the University of Warwick FE member, Jozef Lewandowski, who are empowered to act as required under the guidance of the FE.

2.2   *Facility Management Team*
    The University of Warwick local team supporting the Millburn House Magnetic Resonance Laboratory can organise support & contingency plans for any disruptive events.

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 grant application, Yaroslav Khimyak, UEA, is in place.

3.   **EQUIPMENT FAILURE: Likelihood Medium-High / Impact Low-Medium / Risk rating Medium**
    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.
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   10) Key Performance Indicators (KPIs) and Service Level (SLs) (max. 2 pages)

==For the reporting period, please provide evidence of the facility's performance against its Key Performance Indicators and Service Levels. This information should 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 an explanation and describe the steps taken to mitigate negative impact on users and measures taken to improve performance.==

Data below corresponds to 1st July 2019 to 31st August 2020 (see #6 for explanation of these dates)

QUERY LOG			
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.			
	Queries	Replied within 5 working days	% Replied within 5 working days
Queries from users (email threads, time for response, not FE)	386	386	100%
Fast-track applications by existing users (time for acknowledgement)	1	1	100%
Fast-track applications by new users (time for acknowledgement)	1	1	100%
PhD travel fund applications (time for acknowledgement)	0	N/A	N/A
conference publicity fund applications (time for acknowledgement)	0	N/A	N/A
grant application feasibility (time for acknowledgement)	13	13	100%
Information emails sent by the Facility to full mailing list	6		

DOWNTIME			
Percentage downtime: <10%, >10% but < 20%, >20%			
Downtime KPI: Percentage downtime over period. Report reasons for downtime, Data reported every 6 months.	days	% of 367 days available*	
spectrometer not useable*	0	0	
maintenance days	4	1	
user granted a compensation day	8	3	
Total	12	4	
* Facility operation was suspended due to COVID from March 21st to May 22nd (61 days)			
COMPLAINTS			
Complaints: The NRF will report the number of user complaints and response times. Data reported every 6 months.			
3 working days for first response, 10 working days to resolve the issue: 95% and above; >90% but < 95%; <90%			
	No of Complaints	First response within 3 days	
	0	N/A	
USER SATISFACTION SCORES: 4; 3; 2	No:	Average score	
	28 (PI) and 21 (users) (see #7)	4.8	
DISSEMINATION EVENTS			
Perform a minimum of one dissemination activity per year	Annual Symposium was cancelled due to COVID*		
* see #4 and #13 for new online modes (notably snapshot videos hosted on youtube as well as a new twitter account) for dissemination of research findings the NRF has set-up			
PUBLICATIONS			
The NRF will report the numbers of publications acknowledging the Facility. Data reported annually.	15 (see #2)		
KPI Number of outputs (per instrument) 15; 12; 10			
RESEARCH OUTPUTS (talks and posters)			
Research Outputs Number of Research Outputs, including talks, posters etc. Data reported annually.	25*		
KPI Number of outputs (per instrument) 50; 30; 20			
* missing of the target this year is explained by the absence of in-person scientific conferences in 2020 due to the COVID pandemic.			

There have been some presentations at online conferences, but this is far less than would otherwise have been.			
OUTREACH TO A WIDER USERBASE			
Number of distinct non-NMR meetings at which research outputs are presented by users. Data reported annually.	9*		
KPI Number of outputs (per instrument) 15; 12; 9			
* missing of the target this year is explained by the absence of in-person scientific conferences in 2020 due to the COVID pandemic. There have been some presentations at online conferences, but this is far less than would otherwise have been.			
GRANT APPLICATIONS FOR ACCESS	Applications		
Number of PIs submitting grant applications for access for which the Facility has provided a technical assessment. Data reported annually	11		
KPI Number of applications 8; 6; 4			

Note that the final two KPIs are new for the current NRF funding.

11) Links

What links does the facility have with other NRFs, institutes, Diamond etc? What international links does the facility have. What plans does the facility have to maintain, increase and strengthen such links? If your facility is based outside of the UK how is this a strength of the facility?

The capability and outputs of the NRF are at the cutting edge and are well-known internationally. 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 (currently Tatyana Polenova, Maryland, USA, and Anne Lesage, Lyon, France), as well as a solid-state NMR spectroscopist from UK industry (Nathan Barrow, Johnson Matthey, has joined the OC in 2020, after the completion of Stephen Byard, Arcinova,'s term under the previous NRF funding) and a user representative, who is an early career researcher and user of the Facility (currently Greg Rees, Oxford). Wider input is provided by an expanded OC under the new NRF funding with three new members having joined the OC in 2020, representing another NRF, a CDT and the Diamond synchrotron, namely, Rik Brydson (SUPERSTEM), Stephen Skinner (Imperial, Materials Characterisation CDT) and Julia Parker (beamline scientist at the Diamond Light Source), with Brydson the OC chair.

Recognising potential strong synergies, the application that resulted in the current NRF funding was supported by the Faraday Institution, the Rosalind Franklin Institute and the Sir Henry Royce Institute for Advanced Materials. Specifically, a number of joint workshops were envisaged throughout the current funding period (2020-2024). While the COVID pandemic has precluded in-person events from taking place, #4 details online training that FE members (Blanc, Liverpool, and Griffin, Lancaster) have provided in 2020 through the Faraday Institution.

The NRF Director and Deputy Director know well other NRF Directors (as facilitated by very useful and beneficial regular EPSRC events bringing together the NRF leadership teams). As an example, advertising of a trial of MestreLab software including NMR data processing capability as run by the UK Physical Sciences Data-science Service (PSDS) was advertised to the high-field NMR community (via email) following a direct email request from the PSDS Director, Simon Coles, Southampton.

The NRF instrumentation at 850 MHz and 1 GHz are integrated into the A Pan-European solid-state NMR Infrastructure for Chemistry-Enabling Access that has been recommended for funding (subject to current contract negotiation) under 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 U. K.) as well as the National High-Field Magnet Laboratory in the U.S.A.

12) Improvements and future plans

The NRF's key role is to provide researchers with access to state-of-the-art instrumentation and 2020 has seen a significant expansion of the Facility's capabilities with the installation of the 1 GHz solid-state NMR spectrometer towards the end of 2020 in its purpose designed laboratory at the University of Warwick: this is the first 1 GHz NMR magnet at field in the UK (as featured in a feature article in Chemistry World, https://www.chemistryworld.com/news/uk-reaches-the-gigahertz-nmr-level-behind-other-nations/4012642.article?adredir=1). This will ensure that UK researchers, in both academia and industry, have access to some of the highest-field solid-state NMR spectrometers currently available worldwide, with access to 1 GHz for users becoming available from early 2021 as commissioning is completed. The system is equipped with a range of probes ranging in diameter from 0.7 to 7 mm, providing users with access to a range of sample volumes and spinning frequencies from 5 to 111 kHz, facilitating a broad range of studies in high-spinning-frequency proton-detected measurements of biomolecules and pharmaceuticals to low-gamma studies of inorganic materials. The range of probes available is expected to be extended further in 2021, with the purchase of an additional very-fast MAS probe (£250k funding from a Core Equipment Award, EP/V03622X/1, tender process is currently underway).

As the 1 GHz system comes online however, significant investment has been maintained in the 850 MHz system. In response to user demands, the FE made the decision to invest in additional probes: specifically, the recent installation of a 1.9 mm HXY probe (procured in 2019 in the previous funding period) and the procurement, in 2020 (with £494k funding from the new EPSRC grant), of an additional 1.3 mm HXY probe, and a 1.6 mm (H/F)XY probe to enhance the Facility's ability to conduct fluorine NMR: the latter purchase is from a new supplier, Phoenix NMR, diversifying the range available to users. In addition, a high-temperature laser heated broad banded 7 mm probe which will enable Facility users to access temperatures up to 1000 K, doubling the temperature range currently accessible. These investments ensure that the Facility offers access to some of the highest static-fields currently available whilst providing a range of probes that allows users to conduct advanced solid-state NMR experiments utilizing a broad range of nuclei under a range of conditions (e.g., temperature, spinning frequency, low E-field). In doing so we ensure that the Facility can support an ever increasing and diverse user base.

As a result of the expansion of the NRF, a second Facility manager Trent Franks has been appointed in 2020 to assist Dinu Iuga in the running of the instruments. Trent's background is in the field of biological solid-state NMR, complementing the Dinu's expertise. This will ensure that, despite the expectation that two groups of users may be present at the Facility on the 850 MHz and 1 GHz instruments at any one time, users will continue to obtain the same degree of support and training, whilst benefitting from the broader experience of the facility management team (FMT). During 2020, the Facilities operation was impacted by the arrival of the Covid-19 pandemic, which resulted in shutdown to all but COVID related research in mid-March. However, measures have been implemented to minimise instrumental downtime, and from June 2019 users with time allocated have been able to mail samples to the Facility where they will be set-up on the spectrometers by FMT, who can either measure or grant remote access to the user so that they can conduct their own experiments using Teamviewer software (see also #6). To ensure efficient operation of the spectrometers applications to the time allocation panel now have the option to specify whether samples can be run remotely, this will enable the local management team to respond to changes in access as a result of Covid-19 and maintain spectrometer operation. Clearly operating under these conditions has placed additional demands on the local management team, but they have been pro-active in facilitating remote usage through the development of automatic tuning systems and sample changers which should become available to users during 2021. Although these will undoubtedly be of benefit in the current climate, the ability to automate experiments confers longer term advantages allowing the automated processing of multiple samples.

13) Website

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 (new in 2020)
The UK High-Field Solid-State NMR Facility (@NrfHf) on Twitter (new in 2020)

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 the appointment of a new Facility Administrator in July 2020 under the current NRF grant, a number of minor operational improvements have been made to the web site including the incorporation of guidance for the new SnapShot video resources (see #4) as well as the setting up of social media platforms. In addition, a revamp, to be implemented in 2021, is planned.

The core development targets associated with the website are:

a) Improve the historic front end of the website by creating a well-defined "shop front" page which will co-ordinate with the newly adopted social medial platforms within the website and reflect the recent expansion of the NRF with the arrival of the new 1 GHz capability.

b) Appropriately reorganise the collection of data from users for example, the visitor check-in process or the accommodation request booking process.

c) Use the data collection & workflow tools within the website to create a smooth booking experience for users and importantly to make 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.

d) Expand the 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 the general public.

Analytics

The identification of needed improvements as well as being able to confirm what already works is and will be driven through the continued use of site analytics (as provided by the University of Warwick web development tools):

Site Hits 1st September 2019 – 31st August 2020

Total Hits	On-Campus Hits	External Hits	Student Hits	Staff Hits	Not logged-in user hits
12,434	400	12,029	55	695	11,684

Top Pages (Total Hits from 1st September 2019 – 31st August 2020)

NRF Front page	4127
Annual symposia	1778
Applications for access	1166
Publications	1025
PhD theses Total	876
Probes	471
Service level Agreement	460
Publicity	393
Travel fund	305
Acknowledgement Total	130
Annual Reports Total	115

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. (EPSRC is looking into being able to link to these online, provide links if you have them too).

From 2016 onwards, the NRF has made available its submitted case studies on its webpage https://warwick.ac.uk/fac/sci/physics/research/condensedmatt/nmr/850/case_studies/ : these describe applications to batteries, microporous materials, pharmaceuticals, plant cell walls and proteins. We present here a new less traditional case study of how NMR works across research areas (I) and an update of one of the earlier case studies on microporous materials to include recent applications (II).

I. The UK High-Field Solid-State NMR NRF: Serving the Physical and Life Sciences

High-field solid-state NMR has applications across a wide range of research areas, including batteries, catalysts, energy materials, and pharmaceuticals in the physical sciences and protein and plant cell wall biochemistry and biophysics with relevance to disease and plant biomass energy. This is reflected in a userbase from a wide range of departments spanning Biochemistry, Biological Sciences, Chemical Engineering, Chemistry, Earth Sciences, Life Sciences, Materials Science, Pharmacy and Physics, funded by EPSRC, BBSRC, MRC, NERC and STFC.

As such, NMR is a flagship example for the wider research community coming together. In particular, since its inception, the UK high-field solid-state NMR Facility has played a pivotal role in making the case for joined-up funding across the different research councils through the Facility Executive (FE) that is comprised of eight academics from different UK institutions covering the breadth of solid-state NMR research applications. Specifically, building upon a 2013 EPSRC report by FE member, Mark Smith (then at Lancaster), entitled "Understanding the Current Portfolio and Resourcing Implications of NMR Infrastructure Underpinning World Class Physical Sciences" [1], NMR was the first research area for which EPSRC produced a roadmap in 2013: "Roadmap to provide Internationally Leading NMR Infrastructure for UK Physical Sciences" [2]. Moreover, close working together between NMR spectroscopists in the physical and life sciences led to a "A UK-wide cross-disciplinary integrated infrastructure for NMR spectroscopy" in 2015 and an update of the review by Smith in 2017: "Understanding the Current Portfolio and Resourcing Implications of NMR Infrastructure Underpinning World Class Science in the UK" [4]. The culmination of these efforts was £20M UKRI investment in 2018 in high-field NMR infrastructure [5] including the 1 GHz solid-state NMR spectrometer at the high-field solid-state NMR NRF that in 2020 became the first 1 GHz NMR magnet at field in the UK (see feature article in Chemistry World [6]).

The working together of the distinct physical and life science NMR communities is exemplified by the Connect NMR UK: A National NMR Network for the Physical and Life Sciences network grant (EP/S035958/1) led by FE member, Frédéric Blanc, Liverpool, with co-Is, Christina Redfield, Oxford, and Craig Butts, Bristol [7]. The Network spans three main existing interdisciplinary communities and two learned societies encompassing virtually all UK NMR scientists. Here, the UK High-Field Solid-State NMR NRF provides high-profile representation for the UK solid-state NMR community, with the annual 1-day symposium in March-April being a focal point for exchange of knowledge and viewpoints. The other communities brought together by the Network are the liquid-state, biological NMR community (who are brought together by the MRC-funded Collaborative Computational Project in NMR, CCPN www.ccpn.ac.uk) and the UK-NMR managers group community (UKMRM) which connects industrial and academic NMR facility managers. These communities also hold regular meetings to promote collaboration and outreach, and to share best practice and exchange knowledge. The learned societies comprise the RSC NMRDG, an RSC Interest Group aiming to further scientific understanding and applications of NMR spectroscopy and which organises three 1-day meetings in March-April (thematic meeting), June (postgraduate spring meeting, held the day after the UKMRM meeting) and in December (general meeting); the BRSG: the Magnetic Resonance Group of the IOP aimed at fundamental developments in magnetic resonance techniques, and their applications, which holds an annual 1-day December meeting. The UK High-Field Solid-State NMR NRF links directly to the activities of these societies, with Facility users regularly speaking at their meetings and FE member John Griffin and NRF Technical Director Dinu Iuga being current members of the BRSG committee. As such, the UK High-Field Solid-State NMR NRF forms one of the cornerstones of the UK NMR community, and the integration of its activities with those of the other parts of the UK NMR community via Connect NMR UK is leading into current efforts to secure funding for the next generation of NMR magnet at 1.2 GHz, with the first instruments brought to field in 2020 in Florence, Italy, and Zurich, Switzerland [6].

[1] https://epsrc.ukri.org/newsevents/pubs/understanding-the-current-portfolio-and-resourcing-implications-of-nmr-infrastructure-underpinning-world-class-physical-sciences/
[2] https://epsrc.ukri.org/newsevents/pubs/roadmap-to-provide-internationally-leading-nmr-infrastructure-for-uk-physical-sciences/
[3] https://warwick.ac.uk/fac/sci/physics/research/condensedmatt/nmr/850/future_investment/a_uk-wide_cross-disciplinary_integrated_infrastructure_for_nmr_spectroscopy_march_2015.pdf
[4] https://epsrc.ukri.org/files/newsevents/news/nmr-infrastructure-in-the-uk/
[5] https://webarchive.nationalarchives.gov.uk/20200930161535/https://epsrc.ukri.org/newsevents/news/nmrequipmentinvestment/
[6] https://www.chemistryworld.com/news/uk-reaches-the-gigahertz-nmr-level-behind-other-nations/4012642.article?adredir=1
[7] https://gow.epsrc.ukri.org/NGBOViewGrant.aspx?GrantRef=EP/S035958/1

II. Exploiting Solid-State NMR to Understand Microporous Materials (updated from 2017)

Microporous materials are an important class of inorganic and inorganic-organic hybrid solids, that include aluminosilicate zeolites, phosphate frameworks and metal-organic frameworks (MOFs). Each of these contain pores and channels of similar sizes to small molecules, and when coupled with their high internal surface area leads to applications in catalysis, drug delivery and in gas storage and separation. A detailed knowledge of the atomic-scale structure is vital to understanding the chemical reactivity of these materials; however, this is challenging owing to the varied type and levels of static and dynamic disorder present. Owing to its sensitivity to the local environment NMR presents an ideal tool for this job, complementary to the diffraction-based approaches that can inform on long-range or average structure. Isotopic enrichment is often used to improve the sensitivity of NMR measurements, but changes in the level and position of enrichment can provide important insight into chemical reactivity and mechanism.

In recent work at the Facility, ^{17}O NMR has been used to understand the distribution of cations in a mixed-metal MOF, (Al,Ga)-MIL-53 (see also Fig. 1).[1,2] This material is particularly interesting owing to its "breathing" behaviour, where it can change its pore volume by up to ~33% upon the interaction with a guest molecule, or with a change in temperature. MIL-53 materials were enriched in ^{17}O either using a cost-effective dry gel conversion reaction, which reduces the amount of water required or a novel steaming approach where a pre-prepared MOF is placed in a Teflon cup inside an autoclave lined with 130 ml of $H_2^{17}O(l)$ and heated at 150 °C. High-resolution ^{17}O MQMAS spectra were able to show that although the cations were mixed in the material, there was some preferential clustering of like cations. This led to the formation of a material with both larger and smaller pores sizes present, and the potential opportunity to control average pore volume using compositional changes in the future. In other work,[3] Blanc and co-workers used ^{109}Ag NMR (with ^{13}C and ^{15}N experiments) to explore the ability of a Ag-based MOF to reversible capture perchlorate. By following the structural changes as a function of time, NMR provided information on the timescale of the process (complete within 70 mins), and measurements of the ^{15}N-^{109}Ag J coupling showed the chemical bonds that were formed and the nature of the binding at the Ag centre.
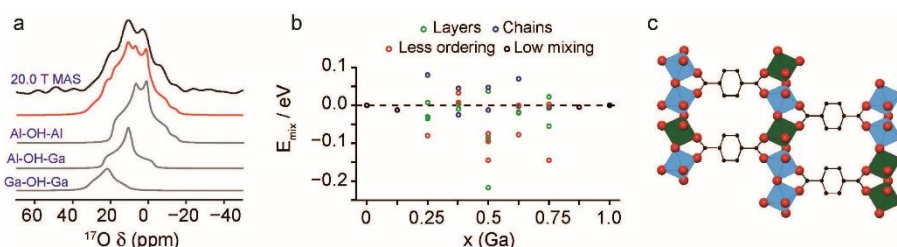

Figure 1. (a) ^{17}O MAS NMR (20.0 T) spectrum of $(Al_{0.5},Ga_{0.5})$-MIL-53 and fit, showing the decomposition into signals resulting from Al–OH–Al, Al–OH–Ga and Ga–OH–Ga species. (b) Calculated mixing energy for the NP form of mixed-metal $(Al_{1-x}Ga_x)$-MIL-53, plotted as a function of composition. (c) Proposed structure mixed-metal MIL-53.[1,2]

Although NMR has been widely used to study zeolite structures in the past, work at the Facility has demonstrated its use for studying chemical reactivity in these systems. In 2019, Ashbrook and co-workers demonstrated the very surprising lability of zeolite frameworks at room temperature when exposed to water.[4] Simply mixing a small amount of the zeolite with 100 ml of $H_2^{17}O(l)$ showed ^{17}O enrichment of the Si-O-Si and Si-O-Al framework oxygens in a CHA zeolite on rapid timescales (1-24 hours) suggesting that the bonds were reversibly and rapidly breaking and reforming, challenging the widely-held notion that zeolites behave largely as inert scaffolds. This investigation built on previous work carried out at the Facility, which also exploited isotopic enrichment (of ^{29}Si and ^{17}O), to explore the mechanism of the ADOR (Assembly, Disassembly, Organisation and Reassembly) process, where new zeolites are produced by disassembling a known parent zeolite into its constituent parts, then organising these in a different way before reassembling to form a new structure.[5,6] Blanc and co-workers also used isotopic enrichment to investigate the intermediates formed in zeolite catalysis.[7] The reaction of zeolite H-ZSM-5 with ^{13}C enriched methanol allowed ^{13}C NMR spectroscopy (including challenging ^{13}C-^{13}C correlation experiments) to probe the mechanism of the methanol-to-olefin reactions, widely used in industry for the production of olefins (mainly ethylene and propene) from non-petrochemical resources such as coal or natural gas. In addition, ^{13}C–^{27}Al and ^{29}Si–^{13}C experiments were able to probe the interactions between the confined carbon species and the framework of the zeolite, confirming the presence of supramolecular reaction centres that are highly efficient for methanol activation.

Work at the NRF in 2020 investigated disorder in a novel gallophosphate framework using multinuclear NMR spectroscopy.[8] This material, GaPO-34A, was shown to form under the same synthesis conditions as GaPO-34, but at shorter gel aging times.[8,9] Diffraction showed a complex average structure, but an NMR crystallographic approach, combining ^{13}C, ^{19}F, ^{31}P and ^{71}Ga NMR spectroscopy with extensive first-principles calculations on a suite of structural models, was able to show that the structure contains at least three distinct types of disorder (occupational, compositional, and dynamic). NMR confirmed the preferential substitution of F onto 3 of the 5 possible anion sites, and also demonstrated ms dynamics of the structure directing agent that balances this charge. This is a particularly challenging structure to solve and this work clearly demonstrated the need to combined different techniques to provide information on the time-scales and length-scales required.

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2. C. M. Rice *et al.*, *Phys. Chem. Chem. Phys.* **22**, 14514 (2020)
3. I. R. Colinas *et al.*, *Dalton Trans.* **46**, 5320 (2017)
4. C. J. Heard *et al.*, *Nature Commun.* **10**, 4690 (2019)
5. G.P.M. Bignami *et al.*, *J. Am. Chem. Soc.* **139**, 5140 (2017)
6. S.A. Morris *et al.*, *Nature Chem.* **9**, 1012 (2017)
7. D. Xiao *et al.*, *Chem. Sci.* **8**, 8309 (2017)
8. S. E. Ashbrook *et al.*, *Inorg. Chem*. **59**, 11616 (2020)
9. L. K. Broom *et al.*, *Dalton Trans.* **46**, 16895 (2017)