Final Report GR/M35789/01

JREI Modern Solid State NMR Console for Materials Characterisation

Overview and Context of Research Programme

This JREI project was to upgrade a then 14 year old console of the 8.45 T instrument of the solid state NMR group at Warwick to state of the art. This was necessary to keep the medium field facilities competitive and means that the modern suite of instruments at the Warwick group's disposal with fields ranging from 4.7-16.6 T are at the leading edge internationally. The instrument played two distinct roles during the project. One was part of the NMR centred programme of the NMR group itself that sought to extend the technique and develop novel applications in understanding inorganic materials. The other was as part of the characterisation facilities available to the collaborating research groups, both within the Physics Department and external, that serviced an extremely wide-ranging programme of materials-centred research. To better understand materials, collecting characterisation data is necessary using a range of techniques. Solid state NMR provides atomic scale, element specific information about local coordination which is helpful in almost all materials problems. There is especial advantage when long-range order is lacking (e.g. amorphous and atomically disordered materials) and standard characterisation techniques provide relatively little information. Often materials can be complex mixtures of crystalline and amorphous components and techniques that provide information about all parts of the sample are essential to obtain full, detailed characterisation. The research programme carried out on the new instrument detailed below illustrates some of the wide range of materials that can benefit from atomic scale study. Solid state NMR as a front line characterisation tool for materials has now been developing for ~20 years. However innovations and applications continue to develop apace so that the volume of solid state NMR research relentlessly expands, with the number of papers having it as the primary physical probe technique increased by a ~1/3 from 1995 to 2000. Inspection of any materials chemistry journal immediately shows that solid state NMR also forms a component of the overall characterisation methodology in many studies. The UK has a very high reputation in solid state NMR with a number of high profile, active groups. The work carried out here forms part of the overall effort, with emphasis on understanding disordered inorganic materials.

Improvement to Infrastructure

The new console improved both the reliability and, through the higher signal-to-noise (S/N) figure of the modern electronics, greatly enhanced the efficiency of the 8.45 T instrument. The higher S/N improved the quality of ^{13}C, ^{17}O and ^{29}Si spectra that were obtained, and meant that some experiments on low-γ (small magnetic moment) nuclei, that were not envisaged in the original proposal, became feasible even at medium field. This included ^{109}Ag in some ceramic glaze samples[58] and $^{47,49}Ti$ NMR to supplement the high field data.[22] However the major improvement was the ability to implement a range of modern pulse sequences requiring rapid switching, shaped high power rf pulses, and accurate fine rf-phase control which would have been very difficult or impossible on the old console. Two-dimensional multiple quantum (MQ) sequences for the improvement in resolution of half-integer spin quadrupole nuclei (which form a large fraction of Warwick's solid state NMR research programme) have become one of the most important NMR methods for studying such nuclei in the solid state. The major drawback of these sequences is their relatively poor sensitivity because of the need to excite MQ transitions. In the last few years there has been a major effort to tackle this sensitivity problem and a plethora of schemes have been suggested. Many of these, such as high power Gaussian pulses, would not have been possible on the old console. We have also experimented with various modulation schemes and in collaboration with Dr Madhu and Prof. Levitt (University of Southampton) have implemented trains of $X\bar{X}$ modulation pulses to redistribute spin populations amongst the satellite transition energy levels to enhance the population differences both for single and MQ experiments. These sequences are easy to set up and have a broadbanded response with respect to the quadrupole interaction, so now are routinely used within our laboratory where enhancement of the S/N for nuclei such as ^{17}O is an extremely important gain.

Scientific Outcomes

Some work was carried out on all the 10 project areas outlined in the original case but space does not allow details for all these to be given so the list below connects these areas (1-10) with the resulting research outputs. Four exemplars then are described in more detail. The programme of work evolved during the project and new research topics (11-16) are also listed where the console played a role and are connected to the listed outputs.

Overview of Projects to which Spectrometer Contributed

1. Amorphous oxide materials *7,8,12,23,34,35,36,38,48,52,66,69,71 (= ref on IGR form p4-6 or at end of report)*
2. Structure of glasses *2,5,10,14,16,24,25,26,29,50,54,57,59,61,62,63,67,70*
3. Dynamics of glasses *15,38,60,73*
4. Zeolite catalysts and related materials *3*
5. High temperature superconductors *4,20,28*
6. Ceramic fibres via sol-spinning and pyrolysis *30,32,56*
7. Clays and calcinations processes *27,39*
8. Alkali metal doped zeolites *1*

9. Fullerene derivatives
10. Nanoporous membranes for gas selectivity, sensing or optical applications *74,75*
11. Ceramic and metallic pigment coatings *49,53,58,65*
12. Piezoelectric ceramics *37,51,64,68*
13. Crystalline materials *6,11,13*
14. VPO catalysts and surface acidity of catalysts
15. Development of low-γ nuclei *17,22,34,35,72*
16. ^{17}O as a probe of hydrogen-bonding of materials *37,55*

Detailed Description of some Projects

(a) Multifield Observation of Quadrupole Nuclei

Quadrupole nuclei can experience dipolar, quadrupolar and chemical shift interactions. Under magic angle spinning (MAS) the anisotropic dipolar, chemical shift and first-order quadrupole interactions are averaged to leave second-order quadrupole effects. However there is increasing interest in nuclei where the quadrupole interaction can be so large that MAS is relatively ineffective and static spectroscopy is used. A particular class of nuclei where there has been much recent interest are low-γ quadrupole nuclei[17] such as titanium. Over the last 3 years we have carried out extensive studies of titanium[22,72] driven by the access to fields up to 14.1 T. This has enabled us to build up the most extensive data set of titanium NMR interaction parameters to date and has allowed the shift ranges for TiO_4, TiO_5 and TiO_6 units to be established. The electric field gradient (efg) at the titanium site showed a strong correlation with the distortion index at the titanium site, allowing identification and assignment of different sites within structures (e.g. $Ca_4Ti_3O_{10}$). Combining the NMR measurements with calculations from the WIEN97 code showed that there is now sufficient accuracy that in cases where there is a significant discrepancy between experiment and calculation it is probable that the crystal structure is not sufficiently accurate and should be re-examined. The 8.45 T instrument has played a crucial role in this work since although the quadrupole interaction was believed to be dominant (most of the previous NMR had simulated such spectra by simply considering the quadrupole interaction) our work found significant discrepancies in trying to fit the static spectra of the two isotopes to the quadrupole interaction alone. Variable field data (Fig. 1) revealed the source of this discrepancy is chemical shift anisotropy (CSA) which can be a significant and modifies the quadrupole interaction deduced from the spectral simulation.

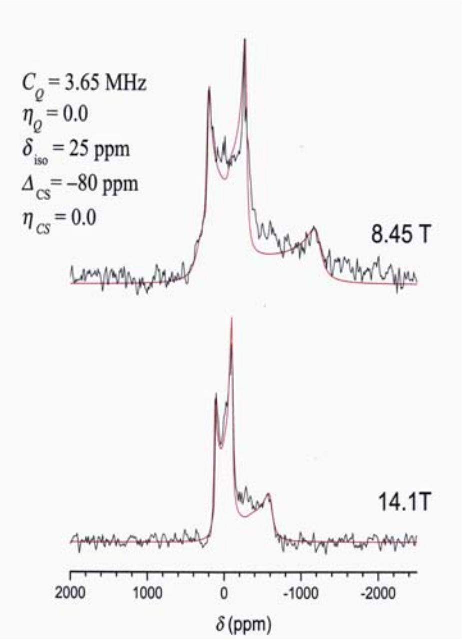

Figure 1. Static titanium NMR data on $PbTiO_3$ at 8.45 and 14.1 T showing a fit involving both quadrupole and chemical shift anisotropy.

For quadrupole nuclei the availability of multiple magnetic fields has been invaluable to understand complex overlapping lineshapes from the field variation. An example is ^{27}Al in calcium aluminates[11] where it was seen that oxygen triclusters in $CaAl_4O_7$ increased the efg at the adjacent AlO_4 units. In $CaAl_{12}O_{19}$, where there are 5 distinct aluminium sites (3 x AlO_6, AlO_5 and AlO_4), there was strong overlap between 4 of these sites. Multiple field NMR was the optimum way of extracting the information. The AlO_5 site has an isotropic chemical shift of 20 ppm, in the range usually associated with AlO_6 so that careful interpretation of peaks in this region is necessary. Other application to crystalline materials included new silicon-free mullites such as $NaAl_9O_{14}$[13] and sodium germanates.[6]

The state of the art of this approach was the application of ^{17}O multifield MQ and DOR NMR to siliceous ferrierite.[3] The structure has 10 oxygen sites 9 of which can be resolved despite their covering a shift range of < 15 ppm with quadrupole interactions differing by only 0.4 MHz. This allows new insight for identifying different sites and different proposed structures could be distinguished. To make maximum use of the NMR data it needs to be combined with *ab initio* calculations of the chemical shift and quadrupole interaction. The identification of specific oxygen sites within the structure offers tremendous potential for understanding which oxygen sites are involved in the catalytic activity of these materials.

(b) High Temperature Superconductors

One of the major difficulties in developing a consistent theoretical model of superconductivity in the high temperature superconducting cuprates (HTSC) is understanding the magnetic and electronic behaviour of the hole- and electron-doped HTSC. It is now generally agreed that the hole-doped HTSC have a d-wave superconducting order parameter, show a normal state pseudogap for low hole doping and exhibit a non-Korringa relationship between the Cu spin-lattice relaxation rate and the Cu Knight shift. This non-Korringa behaviour has been attributed to the Cu spin-lattice relaxation rate being dominated by coupling to antiferromagnetic fluctuations. The situation in the electron-doped HTSC,[20] based on $R_{2-x}Ce_xCuO_4$ (R is a rare earth), is not so clear, with conflicting reports concerning the symmetry of the superconducting order parameter and recent (also conflicting) reports that a pseudogap exists (even in the normal state for temperatures up to 300 K). The understanding of the spin dynamics is hampered by the magnetic rare earth atom, which is believed to dominate the spin-lattice relaxation. We have therefore studied the infinite layer electron-doped HTSC, $Sr_{1-x}La_xCuO_2$ which has the advantage that it does not contain magnetic rare earth ions that can affect the NMR data. Furthermore, the superconducting transition temperature, T_c, is much higher (~43 K) than that in the other electron-doped HTSC being similar to optimally *hole*-doped $La_{2-x}Sr_xCuO_4$. The Cu NMR data reveal a Knight shift and spin-lattice relaxation rate *below* T_c that are inconsistent with isotropic s-wave pairing. The Cu spin-lattice relaxation rate in the normal state, however, is Curie-Weiss like and is comparable to that of the optimally and overdoped hole-doped HTSC, $La_{2-x}Sr_xCuO_4$ with a similar T_c, implying that the electron- and hole-doped HTSC have the same dynamical spin susceptibility. The magnitude of the Knight shift indicates that the density of states at the Fermi level is anomalously small when compared with the hole-doped HTSC with the same T_c. This indicates that the size of $N(E_F)$ is of little importance in the HTSC. We find no evidence of the normal state pseudogap that is observed in the hole-doped HTSC. The significantly smaller DOS but comparable dynamical spin susceptibility and symmetry of the superconducting order parameter in this electron-doped material would appear to suggest that the pairing mechanism is mediated by antiferromagnetic spin fluctuations as suggested by some of the models of the hole-doped HTSC.

(c) Sol-Gel Processing of Materials

Applications in materials technology of sol-gel processing are increasing. The structural development from the initial molecular units to the final solid progresses via a number of intermediate, structurally disordered stages. Atomic scale information can therefore be very important for characterisation.

Our particular interest has been to understand the structural modifications that occur to SiO_2 as secondary oxides such as Ta_2O_5 are added.[7] The effect and distribution of the secondary metal influences properties such as catalytic and optical. Understanding the details of the incorporation of the metal ions and how it changes with heat treatment is important to optimise processing and properties. For example for TiO_2 additions, combining NMR with *in situ* diffraction and EXAFS/XANES 4 distinct titanium sites were distinguished. The changes in their relative population with temperature was followed and related to the catalytic properties of the material. For TiO_2-SiO_2 materials it was shown that one particular TiO_4 site was directly responsible for the catalytic activity.

Variable field ^{17}O NMR data (Fig. 2) plays a central role in looking quantitatively at the level of phase separation in TiO_2-SiO_2 systems.[12] It was concluded that absolute quantification of the level of phase separation from NMR was difficult. Nevertheless trends could be readily followed, such as changes with functionalisation of the silicon precursor, and that modification of the titanium precursor with acetylacetone promoted Ti-O-Si formation enhancing homogeneity.

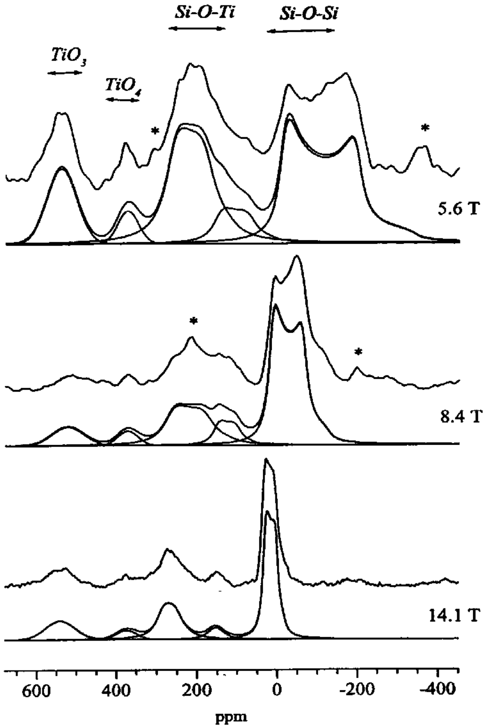

Figure 2. ^{17}O MAS NMR of and Ti/Si gel (with Ti = 33%) produced from alkoxides.

Recent work used a completely multinuclear approach (i.e. ^{1}H, ^{13}C, ^{17}O, ^{29}Si) to examine the effects of different heat treatment schemes and annealing atmosphere on the structure of ternary TiO_2-ZrO_2-SiO_2 xerogel samples.[23] The conclusions were that the equilibrium structure at each temperature was reached rapidly and was largely independent of the heating scheme. The different atmospheres had 2 effects, one was that the loss of the remaining organic fragments and then the residual hydroxyls occurred more readily under air, and the other was that nitrogen preserved the ^{17}O label much more efficiently, the first time this has been properly quantified in the literature.

(d) Studies of Glasses

A wide-ranging programme of applying NMR to glasses was undertaken during the period of the project including cadmium phosphates[19] and borosilicates for high level radioactive waste (HLRW) storage.[16] One application has been to the use of NMR to study the dissolution of volatile species in aluminosilicate glasses. The debate on the effect of e.g. water on the structure has continued fiercely for more than a decade because of the importance of this problem, especially to areas such as the water balance within the Earth and because the properties (e.g. viscosity, density, crystallisation rates) of such glasses and melts significantly change with water-content. As the studies have become more detailed in recent years it has been found that the dissolution mechanism is different in silica-rich compositions from that in the more common aluminosilicate compositions.[10] The ^{29}Si and ^{27}Al parameters varied very little with water-content suggesting that the aluminosilicate framework was little disrupted by water dissolution and that the main effect is alkali cation replacement by a proton. We have used ^{27}Al MQ MAS NMR to determine wether AlOH is formed upon water dissolution as predicted by one group. No AlOH was detected in the glasses investigated indicating that this unit can only be present at a low level.[24] Thus, in agreement with much of the earlier work, the dissolution mechanism does not disrupt the aluminosilicate framework.

^{1}H NMR is potentially a good way of accurately quantifying the H_2O/OH speciation in such systems. The 2 resonances overlap completely so that spectral simulation is necessary. Data was collected at 140K. Lineshapes were a composite of the OH which could be well simulated by a Gaussian, and the H_2O signal which looked like a Pake doublet.[5] However there was some asymmetry to the lineshape due to CSA effects that needed to be accounted for to accurately simulate the lineshape. Carefully chosen experimental conditions are needed to obtain a true undistorted lineshape, in particular it is necessary to use one pulse rather than an echo, with the preacquisition delay as short as possible (no longer than 2 μs) as well as sufficiently long recycle delays of up to 70 s. Under these conditions the NMR determined H_2O/OH ratios agreed very closely with IR data. Hence the methodology developed here should be widely useful for determination of such H_2O/OH speciation.

Research Impact and Benefits to Society

There are several areas that have, and/or will in the future, benefit directly from the research programme that has been carried out with the spectrometer as an important component. There are those condensed matter scientists interested in the structure of inorganic materials including materials scientists, solid-state chemists and mineralogists. There is the background NMR technique development. Titanium is as yet a little studied nucleus, but the data collected here has defined what is currently possible encouraging its more widespread use in understanding materials. There was also the further development of ^{17}O as a probe of nanoscale phase separation, and our work has suggested the optimum strategy for obtaining the most reliable quantitative distribution of oxygen fragments in the structure and hence the level of phase separation. The work on H_2O/OH speciation was the most accurate carried out to date and gave the conditions necessary to ensure quantitative integrity of the spectra. All of these advances in methodology should be useful to a wide range of researchers using solid state NMR to characterise materials.

Some work examined improving properties of materials. For example PbO an important constituent of a range of technologically important glasses but its toxicity has led to legislation to curtail its use, and industries requiring the properties of high lead glasses are exploring alternatives. SnO is a potential substitute and by understanding the structural similarities in detail between these glasses will help speed up this replacement process.[29,46] A similar composition-structure-properties study was carried out on borosilicate glasses aimed at improving the choice of composition best suited for containment of HLRW.[16,25] Other materials technology-oriented projects included studies of pigment coatings and sol-gel processing. All of these areas potentially have direct benefits to society.

This is the type of project at the core of the Materials Programme landscape by developing novel, comprehensive, characterisation in the context of improving understanding of the effects on properties of particular structural characteristics. The interest from the industrial sector in this work is indicated by joint projects that were carried out directly with British industry. This included CASE awards from BNFL on HLRW containment and Johnson Matthey on ceramic and metallic pigments, and catalytic materials.

The contribution of this infrastructure to student training should not be underestimated since exposure to the latest technology is important, especially for those who subsequently follow materials-oriented research careers. During the project 5 PhD students and 1 MSc student completed their theses, with currently another 9 extensively using the instrument, which has also been used by 2 PhD students under a Marie Curie training site grant. 7 postdoctoral research fellows carried out work where solid state NMR was an important component. Also an average of 6 undergraduate students per year make use of the instrument as part of their final year project.

Explanation of Expenditure

Expenditure of EPSRC money was completely as stated in the original grant. The tendering process followed that prescribed by EU regulations and 3 tenders were received. The most competitive was taken. This was for a dual channel Chemagnetics Infinity Plus console. This state of the art instrument was bought with £60k EPSRC funding which represents only 28% of the total cost of the instrument so can be regarded as very good value and good leverage for the EPSRC input. Note that some projects straddled the installation of the console and may have been reported using the former instrument configuration.

Further Research

The research programme of the group has continued to be well supported and has expanded to cover some new areas. Understanding sol-gel structure has continued in TiO_2-ZrO_2-SiO_2 systems (GR/N64151) and was the subject of work carried out by a Marie Curie postdoctoral research fellow. This work has been recently been extended to try and understand the structural foundations of the bioactivity in CaO-SiO_2 gel-produced glasses (GR/R59298). A new area of our work has been to develop fast ^{1}H MAS (GR/R29549) and ^{17}O NMR to study bonding in biomolecular solids with the eventual goal of investigating, for example, hydrogen-bonding in membranes. The exploratory ^{17}O work was partially funded through the award of a Royal Society Leverhulme Trust senior research fellowship to M.E. Smith (2001-2002). More work is planned with Johnson Matthey on catalytic materials to understand the structural basis of acidity. The group was designated a Marie Curie training site in 2001 for solid state NMR of inorganic materials and so far some work on VPO catalysts and copper-based materials has been carried out under this scheme.

Dissemination and Collaboration

The group has undertaken a vigorous programme of dissemination that has included publishing in a range of journals from the leading specialist journals in Chemical Physics/NMR, to those that make direct contact to the target beneficiaries (i.e. materials, glass and Earth scientists). The group regularly contributes to conferences. The regard of the group's work can be gauged by the invitations to give talks at international conferences, as well as a range of colloquia to users of the research outputs (18 in total). A book has appeared[21] and a chapter in an encyclopaedia was written[18] thereby increasing the sources for people seeking background information on the technique.

A whole range of collaborations exist as can be seen from the list of co-authors and papers were published with international co-authors from 8 different groups. Interaction with industry, and those that already exist within the Department has been outlined above. The group firmly believes in applying a comprehensive characterisation methodology to understand complex materials which includes collaborating with experts in other physical methods. These collaborations include with Prof. Newport (Kent, neutrons and synchrotron), Dr Hannon (ISIS, neutrons) and Dr Thomas (Liverpool, Mössbauer). New external collaborations will be established through the Marie Curie funding, and within the Department, a new project with the medical physics group is looking to develop slow MAS to provide chemical information for cell models. Work on the biomolecular materials has initiated collaboration with both the Chemistry and Biology Departments within Warwick, and with Oxford Biochemistry. During the period some initial work was carried out on piezoelectric ceramics[68] (awarded the Laura Marinelli prize) via a Quota PhD studentship. This has now been developed into a full project (GR/R77919) with the ferroelectrics group to provide atomic scale information to better understand the structural source of the physically and technologically interesting properties of ferroelectric materials.

Outputs of Research in which the console played a role (refs 1-21 are the publications on pages 4-6 of the IGR form)

(a) Other refereed journals papers already accepted

22. *Variations of titanium interactions in Solid State NMR - correlations to local* structure, D. Padro, V. Jennings, M.E. Smith, R. Hoppe, P.A. Thomas and R. Dupree*, J. Phys. Chem. B*
23. *The effects of different heat treatment and atmospheres on the NMR signal and structure of TiO_2-ZrO_2-SiO_2 sol-gel materials*, P.N. Gunawidjaja, M.A. Holland, G. Mountjoy, D.M. Pickup, R.J. Newport and M.E. Smith, *Solid State NMR*
24. *Water solubility mechanism in hydrous aluminosilicate glasses: Information from ^{27}Al MAS and MQMAS NM*R, D. Padro, B.C. Schmidt and R. Dupree, *Geochim. Cosmochim. Acta*

(b) Other refereed conference papers already accepted

25. *Boron speciation in waste simulant doped borosilicate glasses using multinuclear MAS NMR*, A. Duddridge, D. Holland, S.M. Dixon and C.R. Scales, *Phys. Chem. Glasses*
26. *Influence of the borate anomaly on the Sn(II) environment in tin borate glasses*, D. Holland, M.E. Smith, A.P. Howes, T. Davis and L. Barrett, *Phys. Chem. Glasses*

(c) Unrefereed conference papers already accepted

27. *Structural evolution of clay minerals on firing deduced from solid state NMR, XRD and TEM*, C.J. McConville, G.E. Roch, W.E. Lee and M.E. Smith, Proceedings 10th International Ceramics Congress, Part E

(d) Papers currently submitted

28. *Carrier concentration-independent antiferromagnetic spin fluctuations in the electron doped high temperature superconducting cuprate, $Pr_{2-x}Ce_xCu_2O_4$*, G.V.M. Williams, S. Kramer, R. Dupree and A.P. Howes, *Phys. Rev. B*
29. *Lone pair effects and structural trends in xSnO.(1-x)P_2O_5 glasses deduced from ^{31}P and ^{119}Sn NMR,* D. Holland, A.P. Howes, M.E. Smith and A.C. Hannon, *J. Phys.:Condensed Matter*

(e) Invited conference presentations

30. *Novel mullite fibre development*, M H. Lewis, Amer. Ceram. Soc. Conf. on Eng. Ceramics, Cocoa Beach, USA, 1/00
31. *Solid State NMR in Minerals and Mineral analogues: current possibilities*, R. Dupree, BRSG meeting NMR Applications in Earth Sciences Cambridge, 3/00
32. *Novel mullite fibre development*, M.H. Lewis, French Materials Soc. Annual Conf., Paris, 10/00
33. *Combining Advanced probe techniques to characterise ceramic materials* (Plenary), M.E. Smith, Annual Ceramics Convention, Cirencester, 4/01
34. *Development of high field ^{47,49}Ti and ^{17}O NMR to study crystallisation, phase separation, and phase composition of nanoparticles*, R. Dupree, 43rd Rocky Mountain Conference On Analytical Chemistry, Denver, 7/01
35. *Recent developments in solid state NMR of quadrupolar nuclei*, M.E. Smith, BRSG meeting overview of recent developments in NMR, London, 11/01
36. *Recent advances and applications of solid state NMR to the characterisation of inorganic materials*, M.E. Smith, ANZMAG meeting, Lake Taupo, 2/02
37. *Solid State NMR of quadrupolar nuclei:- from electroceramics to hydrogen bonding of biomolecules*, R. Dupree, Wilhelm-Ostwald Institute of Physical and Theoretical Chemistry, Universität Leipzig, Germany, 4/02
38. *Applications of solid state NMR in characterising the structure and dynamics of complex materials – emphasis on ^{17}O* M.E. Smith, RSC Solid State Chemistry Group meeting atomic transport in complex materials, London, 6/02
39. *Structural evolution of clay minerals on firing deduced from solid state NMR, XRD and TEM*, C.J. McConville, G.E. Roch, W.E. Lee and M.E. Smith, 10th International Ceramics Congress, Florence, 7/02

(f) Invited colloquia

40. *Solid state NMR as a characterisation tool of inorganic materials*, M.E. Smith, Physics Institute, University of Tartu, 9/00
41. *Solid State NMR: where are we now?* R. Dupree, Tag der Magnetischen Resonanz, University of Stuttgart, 4/01
42. *Solid State NMR: where are we now?* R. Dupree, National Institute of Chemical Physics, Tallinn, 5/01
43. *Solid state NMR as part of an advanced characterisation methodology of materials*. M.E. Smith, MSSI workshop in structural materials and interfaces, University of Limerick, 9/01
44. *Solid state NMR as part of an advanced characterisation methodology of materials*, M.E. Smith,

Department of Engineering Materials, University of Sheffield, 11/01

45. *Recent advances and applications of solid state NMR to characterisation of inorganic mate*rials, M.E. Smith, Department of Chemistry, University of Aberdeen, 11/01
46. *Lone pair cations in glasses*, D. Holland, Department of Chemistry, University of Aberdeen, 11/01
47. *Recent advances and applications of solid state NMR to the characterisation of inorganic materials*, M.E. Smith, IRL Wellington, New Zealand, 2/02

(g) Contributed conference talks

48. *^{17}O solid state NMR characterisation of Si-O-Ti linkages*, M.E. Smith, BRSG meeting NMR applications in Earth Sciences, Cambridge, 3/00
49. *Solid state NMR characterisation of vanadium doped pigments*, N. Dajda, M.E. Smith, N. Carthey and P.T. Bishop, Annual Ceramics Convention, Cirencester, 4/01
50. *Tin germanate glasses*, D. Holland, M.E. Smith, I.J.F. Poplett, J.A. Johnson, M.F. Thomas and J. Bland, NCM8, Aberystwyth, 7/01
51. *NMR Studies of Lanthanum Modified Lead Titanate*, A Baldwin and R Dupree, BRSG meeting overview of recent developments in NMR, London, 11/01
52. *The effect of different heat treatment on the evolution of structural properties of TiO_2-ZrO_2-SiO_2 xerogels*, P. Gunawidjaja, M.E. Smith, M.A. Holland, G. Mountjoy and R.J. Newport, BRSG meeting overview of recent developments in NMR, London, 11/01
53. *Solid state NMR studies of doped zircon pigments*, N. Dajda, M.E. Smith, N. Carthey and P.T. Bishop, BRSG meeting overview of recent developments in NMR, London, 11/01
54. *Influence of the borate anomaly on the Sn(II) environment in tin borate glasses*, D. Holland, M.E. Smith, A.P. Howes, T. Davis and L. Barrett, IVth International Borates Conference, Cedar Rapids, July 2002
55. *Solid state ^{17}O NMR of organic materials – characterisation of hydrogen-bonding*, M.E. Smith, R. Dupree, K.J. Pike, A.P. Howes, A. Kukol, A. Watts, V. Lemaitre, and A. Samoson, Rocky Mountain Symposium on Solid State NMR, Denver, 7/02

(h) Contributed conference posters

56. *Novel mullite fibre development*, D.N. Horspool, M.H. Lewis, C. Freeman and I.C. Alexander, Mullite 2000, Oban, 8/00
57. *Characterisation and radiation resistance of a mixed-alkali borosilicate glass for HLW vitrification*, J.M. Roderick, D. Holland, and C.R. Scales, MRS, Boston, 11/00
58. *Solid State NMR studies of ceramic and metallic coatings*, N. Dajda, M.E. Smith, N. Carthey and P.T. Bishop, Rocky Mountain Symposium on Solid State NMR, Denver, USA, 7/01
59. *Density-structure relations in mixed-alkali borosilicate glasses by ^{29}Si and ^{11}B MAS NMR*, J.M. Roderick, D. Holland, A.P. Howes, C.R. Scales, NCM8, Aberystwyth, 7/01
60. *NASIGLAS structure and properties*, A. Niyompan and D. Holland, NCM8, Aberystwyth, July 2001
61. *Structural implications of water and boron dissolution in albite melts and glasses*, B.C. Schmidt, N. Zotov and R. Dupree, 79. Jahrestagung der DMG, Potsdam, 9/01
62. *Boron and water incorporation mechanisms in aluminosilicate glasse*s, B.C. Schmidt, N. Zotov and R. Dupree, PAC RIM IV, Advanced Ceramics and Glasses, The American Ceramic Society, Maui, Hawaii, 11/01
63. *Structural influence of water dissolution in melts and glasses along the join reedmergnerite – albite*, B.C. Schmidt and R. Dupree, 9th International Symposium on Experimental Mineralogy, Petrology and Geochemistry, Zurich, 3/02
64. *An investigation in the local atomic structure in the non-linear optical material potassium titanyl phosphate ($KTiOPO_4$)*, A. Baldwin, R. Dupree and P. Thomas, IOM Materials Congress, London, 4/02
65. *Solid state NMR studies of doped zircon pigments*, N. Dajda, M.E. Smith, N. Carthey and P.T. Bishop, IOM Materials Congress, London, 4/02
66. *The effect of different heat treatment and atmosphere on the NMR signal and structure of TiO_2-ZrO_2-SiO_2 xerogels* P.N.Gunawidjaja, M.E.Smith, M.A.Holland, G.Mountjoy and R.J.Newport, IOM Materials Congress, London, 4/02
67. *Boron speciation in waste simulant doped borosilicate glasses using multinuclear MAS NMR*, A. Duddridge, D. Holland, S.M. Dixon and C.R. Scales, IVth International Borates Conference, Cedar Rapids, 7/02

68*. *An NMR investigation of lanthanum and zirconium substitution into lead titanate ceramics*, A. Baldwin and R. Dupree, Rocky Mountain Symposium on Solid State NMR, Denver, USA, 7/02
***(Awarded the Laura Marinelli Prize for best poster by a young worker)**

69. *Applications of ^{17}O MAS NMR for characterising silicate-based sol-gel materials*, P. Gunawidjaja, M.E. Smith M.A. Holland, G. Mountjoy, R.J. Newport and D.M. Pickup, Rocky Mountain Symposium on Solid State NMR, Denver, 7/02

(i) PhD these already examined

70. *A characterisation and radiation resistance study of a mixed-modifier borosilicate glass for HLW vitrification*, J.M. Roderick, 2/01
71. *An advanced structural study of amorphous binary oxides of SiO_2 with TiO_2, ZrO_2 and Ta_2O_5*, G.W. Wallidge, 12/01
72. *Solid state NMR study of quadrupole nuclei at high magnetic fields*, D. Padro,2/02
73. *Fast-ion conducting glass and glass-ceramics for pH sensors*, A. Niyompan, 4/02
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