

Program

National Ultrahigh-Field NMR Facility for Solids

<http://www.nmr900.ca>

5th Annual Solid-State NMR Workshop

May 29, 2010, Metro Toronto Convention Centre, Toronto, Ontario

Session 1 (MTCC, Room 203B)

Chair John Ripmeester (NRC Canada)

- 13:00-13:30** **Scott Kroeker** (University of Manitoba) "Further Adventures with ^{73}Ge NMR of Solids: Halides and Oxides"
- 13:30-14:00** **Andre Sutrisno** (University of Western Ontario) "Natural Abundance Solid-State ^{73}Ge and ^{67}Zn Wideline NMR Studies at Ultrahigh Magnetic Field"
- 14:00-14:30** **Leigh Spencer** (McMaster University) "Materials for Lithium Ion Batteries: A Solid-State NMR Analysis"
- 14:30-15:00** **Fabien Aussenac** (Bruker France) "Solid-State NMR Dynamic Nuclear Polarization at 263 GHz"

15:00-15:15 **Coffee Break**

Session 2 (MTCC, Room 203B)

Chair Roderick Wasylishen (University of Alberta)

- 15:15-15:45** **Alex Bain** (McMaster University) "Probing Spectra of Big Quadrupoles"
- 15:45-16:15** **Cory Widdifield** (University of Ottawa) "Solid-State ^{127}I NMR Spectroscopy and GIPAW DFT Calculations of Inorganic Iodide Systems: Structure, Symmetry, and 'Beyond Second-Order' Quadrupole-Induced Shifts"
- 16:15-16:45** **Peter Pallister** (Carleton University) " ^{33}S Ultrahigh-Field Solid-State NMR and First Principles Calculations in Various Sulfate Systems"
- 16:45-17:15** **Facility Users Meeting** David Bryce & Victor Terskikh "National Facility user survey results and overview of application procedures"
- 17:15-18:30** **Reception** (MTCC) sponsored by **Bruker Canada**
(<http://www.bruker.com/ca.html>)

Further Adventures with ^{73}Ge NMR of Solids: Halides and Oxides

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Like many low- γ nuclides, ultrahigh-field NMR has opened up new possibilities for ^{73}Ge NMR studies of solids. Our recent work in this area has shown that while high-quality spectral data can generally be obtained with patience, their analysis and interpretation remain challenging. I will present a synthesis of our experimental and theoretical work on crystalline germanates, showing that the ^{73}Ge NMR observables appear to follow trends analogous to those of other main-group oxides. I will also show the results of ^{73}Ge NMR experiments on a series of germanium halides (GeX_2 and GeX_4), collected at both high and moderate fields. Their structural simplicity belies a deeper level of complexity arising from internal spin interactions. Nevertheless, these contrasting systems provide an ample foundation on which to base future structural studies of Ge-bearing solids.

Natural Abundance Solid-State ^{73}Ge and ^{67}Zn Wideline NMR Studies at Ultrahigh Magnetic Field

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In the past, acquiring NMR spectra of insensitive quadrupolar nuclei was extremely difficult, if not impossible, due to their unfavorable NMR properties (low gyromagnetic ratio (γ), low natural abundance and large quadrupolar moment). However, in recent years, the increasing availability of ultrahigh-field magnets has made the observation of many low- γ quadrupolar nuclei in solids more feasible, even the nuclei of interest are in a non-symmetrical environment.

Here we wish to demonstrate that natural abundance solid-state ^{73}Ge and ^{67}Zn wideline NMR spectra can be obtained at ultrahigh magnetic field of 21.1 T. We report the results of the ultrahigh field study of two representative germanium containing species: GeCl_2 dioxane (a stabilized germylene) and GePh_4 (a prototypical organogermane), yielding the largest ^{73}Ge quadrupolar coupling constant determined by NMR spectroscopy to date and the first direct observation of ^{73}Ge chemical shift anisotropy. We have also characterized the local ^{67}Zn metal centers in several representatives of zinc phosphites- and phosphates-based microporous materials with large pores. Empirical correlations between the measured ^{67}Zn quadrupolar coupling constant and the structural parameters were observed. Quantum chemical calculations of NMR parameters will also be presented in order to assist in explaining the experimental results obtained at the ultrahigh-field.

Materials for Lithium Ion Batteries: A Solid-State NMR Analysis

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Garnet and garnet-like structures have attracted great interest as candidates for solid state materials in solid state lithium ion batteries. It has been shown recently that ^{67}Li NMR is a powerful tool for investigating Li^+ dynamics in garnet structures such as $\text{Li}_5\text{La}_3\text{Nb}_2\text{O}_{12}$ [1]. Within this class of materials iron-containing garnet structures, such as $\text{La}_{32}\text{Li}_{16}\text{Fe}_{6.4}\text{O}_{67}$, have been studied. The structure of these iron-substituted garnet structures was established using powder X-ray diffraction, and a single lithium site was observed [2]. However it is known that lithium is difficult to observe using X-rays. To date NMR has not been used to investigate this series of compounds. The solid-state NMR studies presented here show that this compound has multiple lithium sites, indicating structural disorder, or complexity.

Moreover, these sites show significantly different relaxation behaviour, which is due to the different proximities of lithium nuclei to the paramagnetic iron centers. This assessment allows us to predict a new crystal structure for this compound, in which lithium is distributed among the initially predicted lithium sites and on sites where lithium has replaced iron. Analysis using ^{139}La solid-state static NMR was used to support the hypothesis that the lithium in this compound is able to replace iron, and thus form a distribution of lithium and iron sites. In particular, two types of ^{139}La sites have been observed: one of high symmetry, corresponding to lanthanum surrounded entirely by oxygen, and a second distribution of sites, which have a lower symmetry parameter, indicating the influence of a neighbouring iron atom. Several compounds were made with varying Li, Fe and La content. We show here how the distribution among lithium sites changes with varying Li/Fe content, as observed in both the ^7Li and ^{139}La spectra.

References: (1) van Wüllen, L., Echelmeyer, T., Meyer, H.-W., Wilmer, D. *Phys. Chem. Chem. Phys.*, **9**, 2007, 3298-3303. (2) Mazza, D., Abbatista, F., Vallino, M. *Journal of Less-Common Metals*. **106**, 1985, 277-285.

Solid-State NMR Dynamic Nuclear Polarization at 263 GHz

Fabien Aussenac

Bruker BioSpin, Wissembourg, France



Nuclear Magnetic Resonance is an extremely powerful technique for molecular structure resolution which is often limited by sensitivity. Especially when solids sample are concerned, the sensitivity even decreases by two orders of magnitude per unit time. A range of hyperpolarization methods have been developed to enhance the sensitivity in NMR, such as optical pumping, *para*-hydrogen induced polarization (PHIP) and Dynamic Nuclear Polarization (DNP).

In this communication, we present the 263 GHz solid state NMR-DNP spectrometer which combines a high-power gyrotron micro-wave source and a specialized DNP/NMR low temperature MAS probe (100 K). By transferring the magnetization from electron spins to the nuclear spins, signal enhancement factor of *ca.* 70 can be achieved. A detailed description of the 263 GHz NMR-DNP spectrometer components will be given. We also present recent solid state NMR-DNP applications on biological sample, including for instance membrane protein and amyloidogenic peptide nanocrystals studies.

Probing Spectra of Big Quadrupoles

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We have been developing a simple and systematic way of calculating the complete statics and dynamics of any spin system without approximations. The method is based on the approach that we can deal with the observables in a spin system directly, without having to calculate the wavefunctions first. These observables (usually collected in the density matrix) are obtained from the eigenvalues and eigenvectors of the Liouvillian matrix. Provided we can calculate all the matrix elements of the Liouvillian, we have an exact description of the spin system. In a talk at the main conference, I will be describing this formalism itself, which is based solely on the angular momentum properties of the system – details of the wavefunctions and operators are not needed. For the workshop I will be applying this very general method to simulated spectra of quadrupolar nuclei, in order to probe the applicability of the standard second-order perturbation theory.

Solid-State ^{127}I NMR Spectroscopy and GIPAW DFT Calculations of Iodide Environments in Inorganic Compounds: Structure, Symmetry, and 'Beyond-Second Order' Quadrupole-Induced Shifts

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We have performed solid-state NMR (SSNMR) experiments in standard ($B_0 = 11.75$ T) and "ultrahigh" (21.1 T) magnetic fields on a series of Group 2 metal iodides (MgI_2 , CaI_2 , SrI_2 , BaI_2), selected hydrates ($\text{SrI}_2 \cdot 6\text{H}_2\text{O}$, $\text{BaI}_2 \cdot 2\text{H}_2\text{O}$), and the semiconductor CdI_2 . These experiments have allowed us to measure a broad range of ^{127}I quadrupolar coupling constants (e.g., $C_Q(^{127}\text{I})$) values range from 43.5 MHz in CaI_2 to 214 MHz for one site in SrI_2). Although all of the observed central-transition spectra are dominated by quadrupolar broadening, iodine chemical shift anisotropy has been quantified for several samples (Ω values range from 60 ppm in $\text{BaI}_2 \cdot 2\text{H}_2\text{O}$ to 300 ppm in one of the two sites in BaI_2). As well, we have quantified electric-field gradient (EFG) and chemical shielding (CS) tensor principal axis system non-coincidence in MgI_2 , BaI_2 and $\text{BaI}_2 \cdot 2\text{H}_2\text{O}$. With the help of exact theory [1], we have quantified experimental 'beyond second-order' quadrupole-induced shifts in SrI_2 , BaI_2 , and $\text{SrI}_2 \cdot 6\text{H}_2\text{O}$ (ranging from -50 to -450 ppm at 21.1 T). By combining our current observations with those previously made for $^{35/37}\text{Cl}$ [2] and $^{79/81}\text{Br}$ [3], we have identified interhalogen trends in the observed C_Q and δ_{iso} values across the Group 2 metal halides.

All experimental observations are supported with gauge-including projector-augmented plane wave (GIPAW) DFT calculations [4]. For most systems, crystal structures are available; hence, correlations between iodine SSNMR observables and structure have been made. As well, we have proposed crystal structures for the two hydrates, based on: (i) observed EFG and CS tensor symmetry via their ^{127}I SSNMR powder patterns; (ii) comparison with likely isostructural analogues; (iii) and GIPAW DFT calculations. With continued development, ^{127}I SSNMR experiments should prove useful as probes of local symmetry, local and long-range structure, diffusion in porous materials, inorganic structure refinement, and in understanding halogen bonding interactions in the solid state.

References: (1) Bain, A.D. *Mol. Phys.*, **2003**, *101*, 3163. (2) Widdifield, C.M.; Chapman, R.P.; Bryce, D.L., *Ann. Rep. NMR Spectrosc.*, **2009**, *66*, 195. (3) Widdifield, C.M.; Bryce, D.L., *J. Phys. Chem. A*, **2010**, *114*, 2102. (4) Clark, S.J.; Segall, M.D.; Pickard, C.J.; Hasnip, P.J.; Probert, M.I.J.; Refson, K.; Payne, M.C. Z. *Kristallogr.*, **2005**, *220*, 567.

^{33}S Ultrahigh-Field Solid-State NMR and First Principles Calculations in Various Sulfate Systems

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Given the low-Larmor frequency of about 3.27MHz/T, a very low natural abundance of 0.75% and being a quadrupolar nucleus ($S = 3/2$; $Q = -6.78 \cdot 10^{-26} \text{m}^2$), ^{33}S is a relatively difficult nucleus to study via solid-state NMR. However, through the use of an ultrahigh-field (B_0 of 21.1T), magic-angle spinning, and the combination of various signal-enhancing techniques such as QCPMG, RAPT, and DFS, the study of ^{33}S becomes increasingly feasible. The use of Gauge Including Projector Augmented Wave (GIPAW) plane wave-based first principles calculations for quadrupolar and shielding NMR parameters in comparison to experimental results offers further insight into the nature of sulfur sites in various sulfate systems. Using first principles calculations (CASTEP) and experimental data the accuracy of predicted NMR parameters are evaluated. As well, the efficacy of relating structural parameters and NMR parameters and the possibility of structural optimization on the basis of calculated and experimental results is discussed. The correlation between calculated absolute isotropic chemical shielding, σ_{iso} , and experimentally determined isotropic chemical shift, δ_{iso} , as well as the correlation between calculated and experimental quadrupolar coupling constant, C_Q , will be shown.