

SYMR 2: Poster: Nuclear Magnetic Resonance - Frontiers and Applications

Time: Monday 16:30–18:00

Location: Poster C

SYMR 2.1 Mon 16:30 Poster C

A novel approach to high-pressure nuclear magnetic resonance in diamond anvil cells — ●THOMAS MEISSNER¹, SWEE KUAN GOH², DAMIAN RYBICKI¹, BENNO MEIER¹, GRANT WILLIAMS³, and JÜRGEN HAASE¹ — ¹Faculty of Physics and Earth Science, University of Leipzig, Germany — ²Cavendish Laboratory, University of Cambridge, United Kingdom — ³Industrial Research, Lower Hutt, New Zealand

In addition to variation of temperature and application of external magnetic fields the electronic properties of many materials may be influenced by application of pressure. The highest pressures can be achieved in diamond anvil cells (DAC) but limited sample size and anvil cell geometry hampered their application in nuclear magnetic resonance (NMR) experiments due to a weak signal-to-noise. Recently we succeeded in improving the sensitivity of NMR measurements in DACs significantly by placing the radio-frequency coil containing the sample in the high-pressure region. Here we report on first high-sensitivity measurements at pressures up to 70 kbar.

SYMR 2.2 Mon 16:30 Poster C

EPR and NMR of Multiferroic $\text{Eu}_x\text{Ba}_{1-x}\text{TiO}_3$ — ●NATALIYA GEORGIEVA¹, ANDREAS PÖPPL¹, ROLF BÖTTCHER¹, MARKO BERTMER¹, JÜRGEN HAASE¹, and ALEX SUSHKOV² — ¹Faculty of Physics and Earth Sciences, University of Leipzig, Germany — ²Physics Department, Yale University, New Haven, Connecticut

We are investigating multiferroic $\text{Eu}_x\text{Ba}_{1-x}\text{TiO}_3$ with different Eu^{2+} concentrations ($x = 1, 0.75, 0.5, 0.25$) using Electron Paramagnetic Resonance (EPR) and Nuclear Magnetic Resonance (NMR) spectroscopy. The ceramic samples exhibit different magnetic and electric properties, depending on their Eu^{2+} concentration. The X- and Q-band EPR spectra show almost isotropic exchange-coupled Eu^{2+} signals. Temperature dependent line broadening effects are observed and differ for various Eu^{2+} concentrations. ¹³⁷Ba NMR spectra were recorded using frequency stepped Hahn Echo experiments and preliminary ⁴⁷Ti/⁴⁹Ti NMR measurements were recorded. The line width of the central ¹³⁷Ba nuclear quadrupole transition shows a striking dependence on the Eu^{2+} concentration.

SYMR 2.3 Mon 16:30 Poster C

Spatial inhomogeneities in optimally doped and underdoped high-temperature superconducting single crystals of $\text{HgBa}_2\text{CuO}_{4+d}$, a ⁶³Cu and ¹⁹⁹Hg NMR study — ●DAMIAN RYBICKI^{1,2}, JÜRGEN HAASE¹, MARC LUX¹, MARTIN GREVEN^{3,4}, GUICHUAN YU⁵, and YUAN LI⁵ — ¹Faculty of Physics and Earth Sciences, Leipzig University, Linnéstraße 5, 04103 Leipzig, Germany — ²Department of Solid State Physics, Faculty of Physics and Applied Computer Sciences, AGH-University of Science and Technology, Al. Mickiewicza 30, 30-059 Krakow, Poland — ³School of Physics and Astronomy, University of Minnesota, 116 Church Street S. E. Minneapolis, MN, 55455, USA — ⁴Stanford Synchrotron Radiation Laboratory, Stanford, CA 94309, USA — ⁵Department of Physics, Stanford University, Stanford, CA 94305, USA

Nuclear magnetic resonance is a very important tool to study high-temperature superconducting cuprates (HTSCs). We present results of ⁶³Cu and ¹⁹⁹Hg NMR of $\text{HgBa}_2\text{CuO}_{4+d}$ single crystals with critical temperatures, $T_c=97$ K and $T_c=74$ K (optimally doped and underdoped, respectively). $\text{HgBa}_2\text{CuO}_{4+d}$ due to its very simple structure and only one Cu lattice site is a model compound for understanding the properties of HTSCs. Measurements of the central and satellite transition lines have been carried out as a function of temperature (20-300 K) and orientation of the external magnetic field, B_0 with respect to crystal axes. From the temperature dependence of the spin shifts, line widths and quadrupole splitting we find a very large spatial variation of the hole density even in these high quality single crystals.

SYMR 2.4 Mon 16:30 Poster C

Modeling NMR and EPR Parameters in the Metal-Organic Framework $\text{Cu}_3(\text{BTC})_2$ — ●NINA VANKOVA and THOMAS HEINE — Jacobs University Bremen, School of Engineering and Science, Bremen, Germany

In the last decade metal-organic frameworks (MOF) have been the subject of intensive research activity due to their tunable porous structure

promoting interesting properties and applications. A very powerful tool for characterization of the complex chemical and electronic structure of these nanoporous materials is magnetic resonance spectroscopy. The interpretative and analytical power of the applied NMR and EPR experimental techniques can be significantly enhanced by supplying a reliable theoretical treatment of the underlying spectroscopic parameters.

We report on the application of density functional theory (DFT) for computing the magnetic resonance properties of $\text{Cu}_3(\text{BTC})_2(\text{H}_2\text{O})_3$ (BTC = benzene 1,3,5-tricarboxylate). The ADF 2008 code with Slater basis sets incorporating relativistic corrections has been used for geometry optimization of the MOF building block. We have performed gas phase calculations modeling both the ground singlet and the excited triple state of the Cu(II) ions from the paddle-wheel unit. The nuclear shielding tensors of C and H forming the BTC linkers, as well as the ESR g- and A-tensors of the Cu(II) ions in the paddle-wheel have been calculated and compared to experimental results from the literature.

SYMR 2.5 Mon 16:30 Poster C

NMR in pulsed magnetic fields — ●BENNO MEIER¹, JÜRGEN HAASE¹, FREDERIK WOLFF-FABRIS², THOMAS HERRMANNSDÖRFER², and JOACHIM WOSNITZA² — ¹University of Leipzig, Institute for Experimental Physics II, Magnetic Resonance of Complex Quantum Solids — ²Hochfeld-Magnetlabor Dresden (HLD), Forschungszentrum Dresden-Rossendorf (FZD)

The first observation of NMR in the pulsed high magnetic field at the Hochfeldmagnetlabor Dresden (HLD), Forschungszentrum Dresden-Rossendorf (FZD) is reported. The new spectrometer that operates at up to 3.0 GHz is described, as well as its implementation in the pulsed field facility. Free induction decays and spin echo experiments on ¹H and ^{63,65}Cu in various magnets will be described and discussed in terms of sensitivity and resolution.

SYMR 2.6 Mon 16:30 Poster C

17O and 63Cu NMR of electron-doped High-Temperature Superconductor $\text{Pr}_{1.85}\text{Ce}_{0.15}\text{CuO}_4$ — ●MICHAEL JURKUTAT¹, GRANT WILLIAMS², DAMIAN RYBICKI¹, and JÜRGEN HAASE¹ — ¹Universität Leipzig, Fakultät für Physik und Geowissenschaften, Postfach 100920, 04009 Leipzig, Germany — ²The MacDiarmid Institute, Industrial Research, P.O.Box 31310, Lower Hutt 5040, New Zealand

We present results of a nuclear magnetic resonance (NMR) study of c-axis aligned powder samples of the electron-doped high temperature superconducting cuprate $\text{Pr}_{1.85}\text{Ce}_{0.15}\text{CuO}_4$. In particular the effect of partial Ni substitution for Cu on ⁶³Cu NMR is investigated as a function of temperature, crystal orientation and Ni substitution. We find Ni-induced broadening of the spectra and temperature-dependent effects on spin-lattice relaxation indicating spin density oscillations about the Ni site. Furthermore we analyse the temperature and field dependence of ¹⁷O NMR spectra showing unexpected resemblances to hole-doped systems.

SYMR 2.7 Mon 16:30 Poster C

Chain Dynamics of Polymers Confined to Ordered Nanoporous Alumina Membranes — CORNELIUS FRANZ¹, ●SALIM OK², FABIÁN VACA CHÁVEZ¹, MARTIN STEINHART^{2,3}, and KAY SAALWÄCHTER¹ — ¹Institut für Physik, Betty-Heimann-Str.7, 06120 Halle, Germany — ²Max-Planck-Institut für Mikrostrukturphysik, Weinberg 2, 06120 Halle, Germany — ³Institut für Chemie, Barbarastr. 7, Universität Osnabrück, 49069 Osnabrück, Germany

Ordered anodic aluminum oxide (AAO) membranes with cylindrical 20-400nm pores are ideal inorganic model components that allow studying polymeric interphases and confinement effects in nanocomposites. Advanced NMR techniques enable characterization of polymer chain dynamics in detail. We report the study of polybutadiene (PB) melts infiltrated into AAO by means of transverse relaxometry (T2) as a qualitative indicator for changes in chain dynamics, and by multiple-quantum NMR for more detailed insights.

PB forms solid nanorods in the nanopores of the AAO. Filling kinetics experiments revealed the conditions under which the pore volume is completely filled and equilibrium is reached. At non-equilibrium

stages, we observed strong deviations from the bulk-like entanglement-induced chain ordering, including much increased chain order and an inhomogeneous response, indicating possible layering effects. After the infiltration equilibrium was reached, the behavior was more homogeneous, but still significantly higher local chain order was detected. Moreover, MQ NMR data indicate a shift of T_g. All observed effects became more pronounced upon reduction of the pore diameter.

SYMR 2.8 Mon 16:30 Poster C

Miniemulsion Polymerization Reactions Observed by Time-Resolved Xe-129 NMR — ●MATHIS DÜWEL, NICOLAS VOGEL, CLEMENS WEISS, KATHARINA LANDFESTER, HANS W. SPIESS und KERSTIN MÜNNEMANN — Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany

In the last years, Xe-129 NMR has found many applications in material science and medicine because of two useful properties of Xenon atoms in NMR: their sensitivity to their environment due to their highly polarizable electron cloud, even without the need for covalent bonds, and the ability of being hyperpolarized. Here, Xe-129 NMR is used in the online monitoring of polymerization reactions. The method allows for the online monitoring of polymerization by reporting quantitatively the composition of the reaction mixture by the chemical shift of hyperpolarized Xe. The hyperpolarized gas is brought into contact with the reaction mixture in an NMR tube in a 7 T-NMR spectrometer by the use of hydrophobic hollow-fibre membranes, allowing for the molecular dissolution of the hyperpolarized Xe into the miniemulsion. Repeated Xe-129 NMR measurements show the time-resolved polymerization process. The depolarized Xe is continuously replaced by the gas flow from the hyperpolarizer. Kinetic data for different reaction conditions (e.g., different initiators) has been determined from the chemical shift of the dissolved Xenon, allowing for the comparison with calorimetric data.

SYMR 2.9 Mon 16:30 Poster C

Transport and high-pressure phase equilibria in mesopores — ●PHILIPP ZEIGERMANN, MUSLIM DVOYASHKIN, JÖRG KÄRGER, and RUSTEM VALIULLIN — Department of Interface Physics, University of Leipzig, Germany

Heterogeneous catalysis in high-pressure environments is a standard process in state-of-the-art industrial chemical synthesis. Micro- and mesoporous materials are widely used as hosts for the catalysts, while educts and products are delivered and removed under high pressure conditions. The supercritical state is here of particular interest because of its superior dynamical properties (low viscosity, no surface tension, high diffusivity).

Despite of its advantages in various applications, high-pressure phase equilibria in mesoporous host materials, and especially their interrelation with transport properties, are still poorly understood. Recently, it was shown that pulsed field gradient nuclear magnetic resonance spectroscopy (PFG NMR) is a particularly suitable tool to probe diffusion properties of sub- and near-critical fluids in mesopores.

A special NMR sample vessel has been constructed which permits to maintain pressures up to 200 bars. In this way it is possible to measure pressure-dependent self-diffusivities of organic compounds solved in su-

percritical solvents, e.g., in carbon dioxide in the bulk state as well as in the mesopores. Some preliminary results on molecular diffusivities at different conditions will be presented.

SYMR 2.10 Mon 16:30 Poster C

Field-cycling-NMR: A new magnet design for reduced energy consumption — ●DIRK PLENDL, ALEXEI F. PRIVALOV, and FRANZ FUJARA — Institut für Festkörperphysik, TU Darmstadt, Hochschulstraße 6, 64289 Darmstadt

Field-cycling-NMR is an established method for the investigation of field dependent spin phenomena, like relaxation dispersion, polarization transfer, enhanced NQR etc. In contrast to normal NMR, the magnetic field in a field-cycling experiment is switched between several distinct levels within milliseconds. This can only be achieved with specially designed, low inductive magnets.

Today, nearly all FC-spectrometers utilize air core coils made of copper or silver. Producing strong magnetic fields with normal-conducting magnets results in a large energy dissipation (tens of kW) so that the maximum field strength is limited by the amount of heat that can be extracted by the cooling system.

We present a new magnet design for fast field-cycling-NMR which uses a magnet with an iron core for field amplification, thus generating the same field with significantly reduced energy consumption and system complexity [1].

[1] D. Plendl, M. Fujara, A. F. Privalov, F. Fujara, J. Mag. Res. 198 (2009) 183-187

SYMR 2.11 Mon 16:30 Poster C

A spatially resolved mechanical field cycling relaxometer — ●MICHAEL DITTER¹, HOLGER STORK^{1,3}, ACHIM GÄDKE^{1,4}, FRANZ FUJARA¹, BEATRICE SCHUSTER^{1,2}, CHRISTINA TRAUTMANN², and REINHARD NEUMAN² — ¹Institut für Festkörperphysik, TU Darmstadt, Hochschulstr. 6, Darmstadt — ²GSF Helmholtzzentrum für Schwerionenforschung, Darmstadt — ³National des Champs Magnétiques Intenses, r. d. Martyrs, Grenoble — ⁴School of Engineering and Computer Science, Victoria University, Kelburn Parade, Wellington

Recently a new method for the spatially resolved characterization of heavy ion irradiated crystals using static field gradient NMR was developed [1]. With this method it is possible to measure one-dimensional spin-lattice relaxation rate profiles with a spatial resolution in the order of 10 μm. In the meantime the spectrometer has been further improved and the method expanded to conduct frequency and temperature dependent measurements. For field cycling NMR the probe is moved inside the stray field of a superconducting magnet. Due to the strong magnetic field gradient only the nuclei within a thin excited slice are in resonance, allowing spatial resolution. It is possible to utilize fields between 6.3 and 0.008 T. The positioning system is capable of achieving switching times of less than 5 s. The accessible sample temperature ranges from RT to 500 K. The relaxometer will be used for spatially resolved spin-lattice relaxation dispersion experiments of swift heavy ion irradiated ionic crystals.

[1] Stork H, Hamburger A, Gädke A, Fujara F and Schwartz K 2008 J. Phys.: Condens. Matter 20 275236