Video Article

High-Sensitivity Nuclear Magnetic Resonance at Giga-Pascal Pressures: A New Tool for Probing Electronic and Chemical Properties of Condensed Matter under Extreme Conditions

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Abstract

Nuclear Magnetic Resonance (NMR) is one of the most important techniques for the study of condensed matter systems, their chemical structure, and their electronic properties. The application of high pressure enables one to synthesize new materials, but the response of known materials to high pressure is a very useful tool for studying their electronic structure and developing theories. For example, high-pressure synthesis might be at the origin of life; and understanding the behavior of small molecules under extreme pressure will tell us more about fundamental processes in our universe. It is no wonder that there has always been great interest in having NMR available at high pressures. Unfortunately, the desired pressures are often well into the Giga-Pascal (GPa) range and require special anvil cell devices where only very small, secluded volumes are available. This has restricted the use of NMR almost entirely in the past, and only recently, a new approach to high-sensitivity GPa NMR, which has a resonating micro-coil inside the sample chamber, was put forward. This approach enables us to achieve high sensitivity with experiments that bring the power of NMR to Giga-Pascal pressure condensed matter research. First applications, the detection of a topological electronic transition in ordinary aluminum metal and the closing of the pseudo-gap in high-temperature superconductivity, show the power of such an approach. Meanwhile, the range of achievable pressures was increased tremendously with a new generation of anvil cells (up to 10.1 GPa), that fit standard-bore NMR magnets. This approach might become a new, important tool for the investigation of many condensed matter systems, in chemistry, geochemistry, and in physics, since we can now watch structural changes with the eyes of a very versatile probe.

Video Link

The video component of this article can be found at http://www.jove.com/video/52243/

Introduction

Since Percy Bridgman's hallmark experiments of condensed matter under high hydrostatic pressures at the beginning of the last century, the field of high pressure physics has evolved rapidly[1]. A large number of intriguing phenomena are known to occur under pressures of several GPa[2]. In addition, the response of condensed matter systems to high pressure has taught us a lot about their electronic ground and excited states[3,4].

Unfortunately, techniques for the investigation of the electronic properties of condensed matter at Giga-Pascal pressures are rare, with x-ray or DC resistance measurements leading the way[5]. In particular, the detection of electronic or nuclear magnetic moments with electron spin (ESR) or nuclear magnetic resonance (NMR) experiments, is bound to be almost impossible to implement in a typical high-pressure anvil cells where one needs to retrieve the signal from a tiny volume enshrined by anvils and a sealing gasket.

Several groups have tried to solve this problem by using complex arrangements, *e.g.,* two split-pair radio-frequency (RF) coils wound along the flanks of the anvils[6]**;** a single or double loop hair-pin resonator[7,8]; or even a split rhenium gasket as a RF pick-up coil[9], see **Figure 1**. Unfortunately, those approaches still suffered from a low signal-to-noise ratio (SNR), limiting the experimental applications to large-γ nuclei such as ^{1}H[10]. The interested reader may be referred to other high-pressure resonant tank circuit experiments[11–15]. Pravica and Silvera[16] report the highest pressure achieved in an anvil cell for NMR with 12.8 GPa, who studied the ortho-para conversion of hydrogen.

With great interest in applying NMR to study the properties of quantum solids, our group was interested in having NMR available at high pressures, as well. Finally, in 2009 it could be demonstrated that high-sensitivity anvil cell NMR is indeed possible if a resonating radio-frequency (RF) micro-coil is placed directly in the high-pressure cavity enclosing the sample[17]. In such an approach, the NMR sensitivity is improved by several orders of magnitude (mostly due to the dramatic increase in filling factor of the RF coil), which made even more challenging NMR experiments possible, *e.g.,* ^{17}O NMR on powder samples of a high-temperature superconductor at up to 7 GPa[18]. Superconductivity in these materials can be greatly amplified by the application of pressure, and it is now possible to follow this process with a local electronic probe that promises fundamental insight into the governing processes. Another example for the power of NMR under high pressure emerged from what were believed to be routine referencing experiments: in order to test the introduced new anvil cell NMR, one of the best known materials was measured – simple aluminum metal. As the pressure was increased, an unexpected deviation of the NMR shift from what one would expect for a free-electron system was found. Repeated experiments, also under increased pressures, showed that the new results were indeed reliable.

Finally, with band structure calculations it was then found that the results are the manifestation of a topological transition of the Fermi surface of aluminum, which could not be detected by calculations years ago, when the computing power was low. Extrapolation of the findings to ambient conditions showed that the properties of this metal that is used almost everywhere are influenced by this special electronic condition.

In order to pursue a number of different applications specially designed anvil cells (previous cells had been imported from the Cavendish Laboratory and retrofitted for NMR) have been developed. Currently, the used home-built chassis are capable of reaching pressures up to 25 GPa using a pair of 800 µm culet 6H-SiC anvils. NMR experiments were successfully conducted up to 10.1 GPa, so far. The NMR performance of this new cells was shown to be excellent[19]. The main component is Titanium-Aluminum(6)-Vanadium(4) with an extra low interstitial level (grade 23), providing a yield strength of about 800 MPa[20]. Due to its non-magnetic properties (the magnetic susceptibility χ is about 5 ppm) it is an adequate material for the anvil cell chassis. The overall dimensions of the introduced cells (see **Figure 2** for an overview of all home-built anvil cell designs) are small enough to fit into regular standard bore NMR magnets. The smallest design, the LAC-TM1, which is only 20 mm in height and 17 mm in diameter, fits also typical small, cold-bore magnets (30 mm bore diameter). The LAC-TM2, which is the latest chassis the authors designed, uses four M4 Allen countersink bolts (made out of the same alloy as the cell chassis) as pressure driving mechanism, allowing for a smooth control of the internal pressure (blue prints attached in supplementary section).

Typically, diamond anvils are used in order to generate highest pressures of above 100 GPa. Xu and Mao[21–23] have demonstrated that moissanite anvils provide a cost effective alternative in high-pressure research, up to pressures of about 60 GPa. Therefore, moissanite anvils were used for the introduced GPa NMR approach. The best results were achieved with customized large-cone 6H-SiC anvils from the anvil department of Charles & Colvard. With those cells, for pressures up to 10.1 GPa, the use of 800 µm culet anvils was found to result in very good NMR sensitivity. For comparison, Lee *et al.* report a SNR of 1 for ^{1}H NMR of tap water, while the SNR of the introduced micro-coil approach showed a value of 25 for 1/7 of their volume, even at a somewhat lower magnetic field.

With this new approach to high-sensitivity anvil cell NMR one can pursue many applications that promise exciting new insight into the physics and chemistry of modern materials. However, as always, sensitivity and resolution ultimately limit the application of NMR, in particular, if one is interested in much higher pressures that demand smaller culet sizes. Then, one has not only to optimize the cell design with even smaller RF coils, but also think about methods for increasing nuclear polarization.

Protocol

1. Mounting and Aligning of the 6H-SiC Large Cone Boehler-type Anvils

1. Fix the piston and x-y plate in the mounting tools and insert the Boehler-type anvils in the seating area.
2. Make sure each anvil sits firmly in the backing plates.
3. Using epoxy resin, (*e.g.*, Stycast 1266), glue both anvils to their seats. Cure for 12 h at RT, or 65 ºC in a furnace for 2 hr.
4. For a sufficient anvil alignment, use the M1 set-screws to align the backing plates and monitor the parallelism of both anvils. If the anvils were found to be non-parallel, remove the epoxy resin and restart at point 1.2.

2. Gasket Preparation

1. Drill 1 mm holes into a chip of annealed Cu-Be (Cu 98 w%, Be 2 wt%, thickness of 0.5 mm) for the brass guide pins.
2. Insert three 5 mm long pieces of 1 mm diameter non-insulated copper wire into the holes, which are distributed along the anvil, to serve as guide pins for the Cu-Be gasket.
3. Check for proper grounding between the guide pins and the cell body. Typically, a DC resistance of about 0.1 Ω is desired. Improve with an application of a small amount of conductive silver.
4. Place the Cu-Be chip on top of the moissanite anvil and close the cell.
5. Using a hydraulic press, pressurize the gasket to about 1/8th of the culet diameter for maximized working stability. Monitor the actual thickness of the indentation using a micrometer caliper.
6. Drill a hole of the appropriate diameter (½ of the culet diameter) in the center of the indentation.
7. Carve two channels into the pre-indented gasket. The channels should be deep enough to accommodate the 18 µm copper wire of the micro-coil.
8. Harden the prepared gasket at 617 K for 2 to 3 hr in a furnace.

3. Preparing and Loading of the Micro-coil

1. Use a piece of 1 mm copper wire and thread it through the feed-through of the piston. Fix the copper wire with epoxy resin and cure it according to step 1.3.
2. Choose an awl (see list of materials) which has the desired diameter for the micro-coil and fix it between a pair of rotatable chuck-jaws.
3. Glue (with *e.g.*, varnish from SCB, see list of materials) one end of the 18 µm copper wire onto the chuck jaws, while holding the other end and rotate the chuck jaw so that the wire is coiled onto the awl.
4. When the micro-coil is of the desired geometry, fix the other end of the wire onto the glue as well.
5. Use diluted varnish to fix the coil by applying a small amount on top of the windings.
6. Remove the coil carefully from the awl using Teflon tape.
7. Place some epoxy resin (see point 1.3), without any additives, in the channels of the gasket.
8. Place the micro-coil inside the sample chamber and fix the leads into the channels.
9. Cure the epoxy resin according to step 1.3.
10. Solder one lead of the micro-coil to the hot wire and the other to a guide pin.
11. Add some silver conductive paste on top of each junction. Curing typically takes some minutes.

12. Seal both junctions with a small amount of epoxy resin.
13. Cure the epoxy according to step 1.3.
14. Now, check the DC resistance of the coil after every step.
15. Place the sample in the micro-coil. Be aware that any unnecessary physical contact may destroy the coil.
16. Add finely ground ruby powder to the sample for pressure calibration.
17. Finally, flood the sample chamber with an appropriate pressure medium. Use paraffin oil to ensure nearly-hydrostatic conditions up to 9 GPa.
18. Close the cell carefully.

4. Applying and Monitoring Pressure

1. At first, slightly tighten the M3 Allen countersunk screws.
2. For pressurization fix the cell in a vise. Now, tighten two opposing screws pairwise.
3. Place the pressurized cell in an appropriate cell holder.
4. Adjust the position of the cell so that the laser beam reaches the sample chamber.
5. Use the fine-adjustment table to focus the ruby powder in the laser beam.
6. Monitor the ruby photoluminescence spectrum using the corresponding spectrometer software.
7. Extract the actual pressure in the sample cavity from the observed spectral shift of the ruby R1 and R2 lines.
8. Equilibrate the pressurized cell for at least 12 hr before NMR measurements are started.

5. Performing NMR Experiments

1. Mount the pressure cell onto a typical NMR probe. Manufacture appropriate cell holders in a mechanical workshop.
2. Solder the hot wire to the probe. Check for proper electrical contact between the cell and the probe.
3. Now, perform standard NMR experiments. Draw attention to the fact that the micro-coil is very sensitive to the applied radio-frequency power.

Representative Results

Figure 3 shows how the completely assembled pressure cell, the wiring, and the mounting onto a typical NMR probe look like. In the following, several experiments will be reviewed which should enable the reader to gather a broad overview about the benefits and limits of the introduced technique.

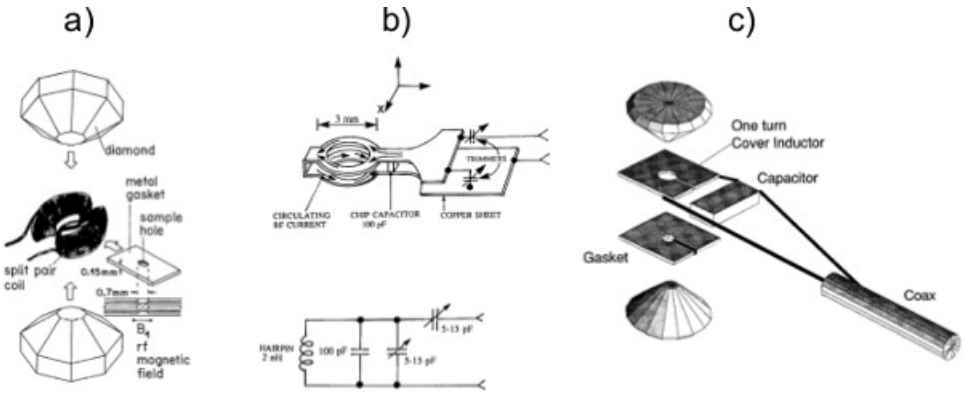


Figure 1. Various Approaches for high pressure NMR: (A) Split pair coil encompassing the anvil flanks as well as a rhenium gasket from Bertani *et al*. (Reproduced with permissions from Bertani *et al.*[4]. Copyright 1992, AIP Publishing LLC.) **(B)** Hair-pin resonator from Lee *et al*. (Reproduced with permissions Lee *et al.*[6]. Copyright 1992, AIP Publishing LLC.) **(C)** Pravica *et al*. introduced a method using a split gasket together with a one turn cover inductor as a radio-frequency pick-up coil. (Reproduced with permissions from Pravica *et al.*[7]) Please click here to view a larger version of this figure.

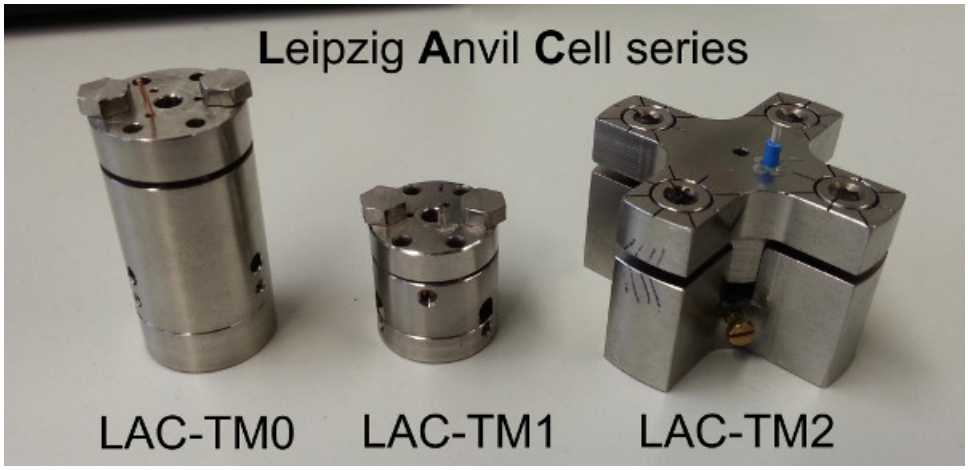


Figure 2. Various high pressure anvil cell designs for NMR: All designed cell chassis consist of a simple piston-cylinder set-up without further anvil alignment mechanisms with exception of a planar adjustable conical anvil backing plate. The cylindrical cells TM0 and TM1 are particularly suitable for NMR investigations of single crystals where a proper crystal alignment can be achieved by rotating the cells along their symmetry axis. The overall dimension of all chassis does not exceed 40 mm, enabling them to be used in standard wide-bore NMR magnets. The dimensions of the smallest design (TM1) enables it to be used even for small-bore magnets (overall dimensions 20 mm x 18 mm).

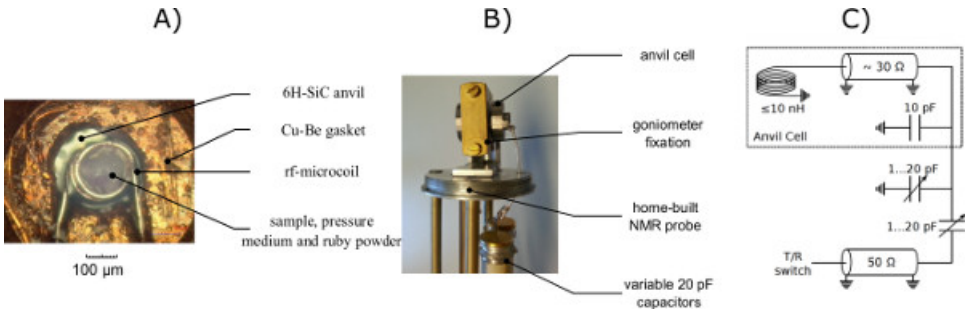


Figure 3. (A) Photograph of the high-pressure region with a 4-turn micro-coil filled with a liquid gallium sample, ruby powder and pressure transmitting medium. **(B)** Mounted LAC-TM1 on a home-built NMR probe. **(C)** Schematic wiring of the probe connecting the micro-coil in the high-pressure region, see also[29]. Please click here to view a larger version of this figure.

I) ^{27}Al NMR of aluminum powder up to 10.1 GPa[24] and ^{17}O NMR of $YBa_2Cu_4O_8$ up to 6.4 GPa[25]

The first experiments were conducted using a Beryllium-Copper diamond anvil cell design from the Cavendish Laboratory at Cambridge University, which was widely used for de Haas-van Alphen measurements[26]. The cell was readied for high-sensitivity NMR experiments in Leipzig and representative results will be discussed now.

The first set of experiments concern the investigation of metallic aluminum that was believed to be a suitable reference compound. Two different anvil cells were used, equipped with anvils of 1,000 µm culet diameter for pressures up to 4.2 GPa, and with anvils of 800 µm culets for pressures up to 10.1 GPa. The corresponding micro-coils were solenoids with 10 turn (300 µm diameter), and 9 turns (200 µm diameter), for the 1 mm and 0.8 mm culet anvils, respectively. The diameter of the insulated Cu wire was 15 µm. The pressure cells were loaded with finely crushed aluminum powder (3N purity, 325 mesh) and a small ruby chip serving as a pressure sensor. As pressure transmitting media, Daphne 7373 and glycerin were used, providing hydrostatic conditions up to at least 5 GPa[27]. NMR measurements were conducted in magnetic fields of 7.03 T, 11.75 T, and 17.6 T at RT (field dependent measurements were necessary to investigate the line broadening mechanism). The quality factor Q of the resonance circuit was about 16 for all cells. With nutation experiments, the π/2 pulse length were determined to be about 2 µs at approximately 1 Watt average RF pulse power. Those parameters lead to an average RF magnetic field amplitude B_1 in the resonating micro-coil of about $B_1=\pi/(2\gamma_n t_{\pi/2})$= 11 mT (the gyromagnetic ratio of ^{27}Al is $6.98\cdot10^7$ radT^{-1}s^{-1}). This estimate is only a factor of 3 smaller than the theoretical figure, $B_1=[(\mu_0 QP)/(2\omega V_{coil})]^{½}$= 35 mT, and shows that most of the RF power indeed drives the Al resonance and good sensitivity for detection can be expected, as well. For example, at 6.3 GPa, 1024 signals were accumulated to give satisfactorily spectra. With a pulse repetition time of approximately 50 ms, the total measurement time was only about 1 min per spectrum. The shifts were referenced to an aqueous $AlCl_3$ sample.

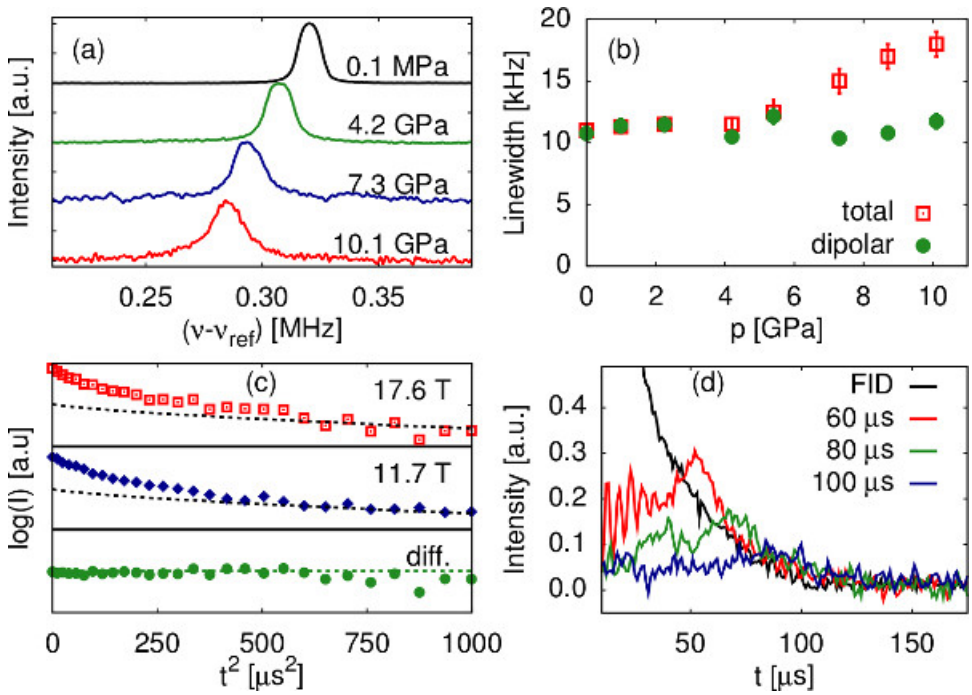


Figure 4. ^{27}Al NMR on metallic aluminum powder: (A) acquired spectra up to 10.1 GPa; **(B)** the observed total line-widths (red squares) increased from about 77 ppm up to 145 ppm at 10.1 GPa; **(C)** recorded free induction decays at magnetic fields of 11.74 T (blue), 17.6 T (red) and the difference between both (green); **(D)** obtained spin echoes at elevated pressure for different pulse separation times. Reprinted **Figure 1** from Meissner *et al.*[23] Please click here to view a larger version of this figure.

The most important result was an unexpected deviation of the Knight shift (1640 ppm at ambient pressure) from the free-electron behavior as the pressure increased. As subsequent band-structure calculations revealed this is due to a Lifshitz transition of the Fermi surface that was hitherto unknown. Additionally an unusual increase of the field-independent line-width at high pressures was discovered that could not be explained yet. It may be caused by a structurally forbidden quadrupole interaction, or it may signal onset of an indirect inter-nuclear magnetic dipole coupling due to the approaching van-Hove singularity. Alternatively pressure gradients may be behind this finding, but since different transmitting media give similar results and with the line-widths being field independent, only deviations from the cubic structure can explain the results.

This example shows that one can even learn important details about well-known systems, information that can be quantitatively tested subsequently leads to the calibration of state-of-the-art computation. For example, since only s-like electrons dominate the shift, we even learn about how they participate in changes at the Fermi surface.

The second set of experiments concerns ^{17}O NMR of the high-temperature superconductor $YBa_2Cu_4O_8$. These experiments were the driving force behind the development of high-sensitivity anvil cell NMR. The temperature-dependent NMR shifts are largely known for this and other superconductors, even for different doping levels. However, since these systems are yet not fully understood, one is interested in having another suitable parameter at hand that one can vary while investigating how it influences the NMR signals. Since it is known that the ^{17}O NMR in these systems is dominated by the electronic spins (and no orbital effects), it lends itself for pressure-dependent studies. Here, anvil cells with 1 mm (2 to 3 GPa) and 0.8 mm (4.2 to 6.3 GPa) culet moissanite anvils were used. The dimensions of the micro-coils were similar to those used for the metal aluminum experiments described above. While the samples were enriched with ^{17}O, such experiments on powder samples are still rather challenging. The measurements were carried out at magnetic fields of 11.75 T at temperatures from 85 K to RT. NMR signals were recorded by accumulating Hahn echoes[28]. By varying the RF pulse power, the π/2- and π-pulse durations were found to be 1.7 μs and 3.4 μs, respectively. The pulse separation was typically 30 μs. At RT, the Q-factor was about 12. The B_1-field was 25 mT at an average RF pulse power of 1 W, in good accordance with the predicted value (43 mT). Usual acquisition times were about 14 hr for one spectrum. This rather long measurement time is due to the relatively low Larmor frequency and the low number of resonant ^{17}O nuclei in the powder sample. Again, these first experiments proved to provide very exciting results. This material ($YBa_2Cu_4O_8$) was the “drosophila” for extensive NMR experiments, earlier. It is a stoichiometric material, but shows the pseudogap feature that is so characteristic for this class of materials, but it is not understood. By applying pressure, the temperature dependence of the shift changes significantly. The pseudogap feature disappears gradually as the pressure increases, similar to what happens if one increases the doping level for other systems. Furthermore, and quite unexpected, it was found that this happens by a change of two shift components: one of them decreases slightly (it has the temperature dependence of the ambient pressure signal), the second component that behaves like that of a metal is hardly visible at ambient pressure, but is tremendously amplified with pressure and dominates the shift at the highest pressure of 6.4 GPa.

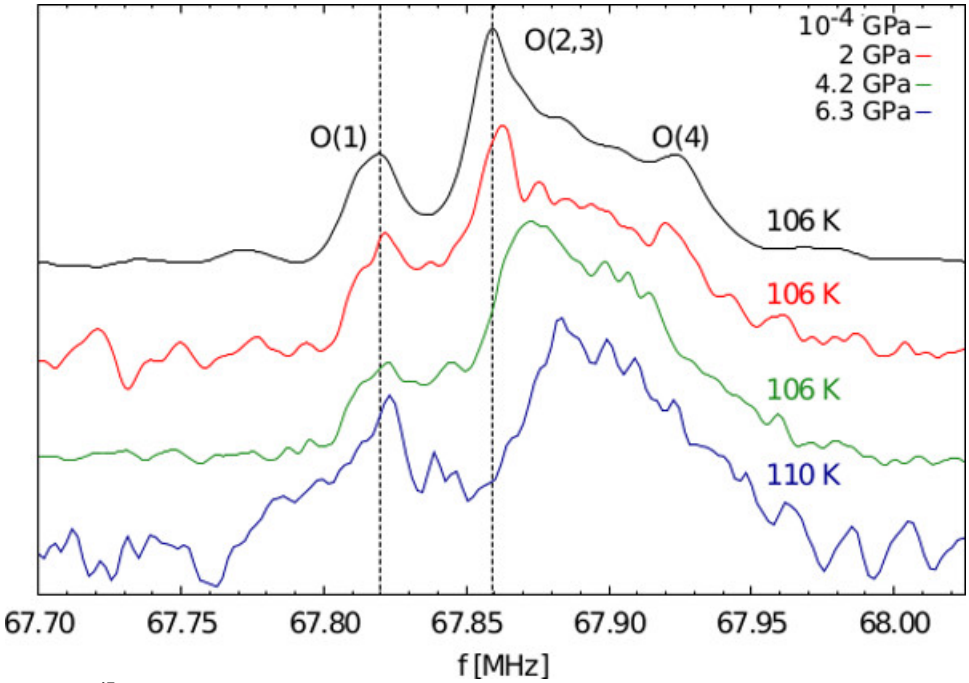


Figure 5. ^{17}O NMR on $YBa_2Cu_4O_8$ up to 6.4 GPa. Upper Panel: Observed 17O NMR spectrum at 6.3 GPa at 110 K. The observed line-width was about 1,500 ppm. Lower: recorded oxygen NMR spectra. Four distinct ^{17}O signals could be identified (stemming from the planar, apex and chain oxygens) even at higher pressures at temperatures between 105 and 110 K. Reprinted **Figure 2** with permission from *Meissner et al.*[24] Please click here to view a larger version of this figure.

With such stunning results the authors decided to engage deeper into designing home-built high-sensitivity anvil cell devices.

II) ^{69,71}Ga-NMR of liquid gallium at 1.8 GPa

In order to quantify the performance of the introduced moissanite anvil cells in more detail, liquid gallium was chosen as a test sample. The liquid gallium sample was obtained with a purity level of 5N. Loading of the micro-coil was achieved by liquifying a small piece of gallium and subsequently filling it into the micro-coil. For obtaining the data shown in this report, no isotopically enhanced sample were used; the natural abundance of the ^{69}Ga and ^{71}Ga isotopes was found to be sufficient.

The liquid state of gallium exists at elevated pressures up to 2 GPa. Therefore, very sensitive high-resolution measurement can be carried out on this system. **Figure 6** shows some typical ^{69,71}Ga-NMR spectra at RT and 1.8 GPa pressure. The measurements were carried out at a magnetic field of 11.74 T using an anvil cell equipped with two 800 µm culet 6H-SiC Boehler-type anvils, and a 4-turn micro-coil of 200 µm inner diameter made of 18 µm diameter copper wire. The Q-factor was about 18 at 120.5 MHz and 150.3 MHz. The lengths of the π/2 pulses were investigated at an average RF pulse power of about 150 mW, and were determined as 3 µs and 2 µs for ^{69}Ga and ^{71}Ga, respectively. The corresponding magnetic field amplitudes were found to be 28 mT and 25 mT in excellent agreement with the estimates. Experimentally, the signal-to-noise ratios were found to be SNR(^{69}Ga) = 0.8 and SNR(^{71}Ga) = 0.5 at a noise bandwidth of 1 MHz. Following the calculations of ref. 19, the expected SNR was calculated to be 1 and 1.2 for ^{69}Ga and ^{71}Ga, respectively. It was estimated that only $4.6 \cdot 10^{16}$ and $3 \cdot 10^{16}$ resonant nuclei for ^{69}Ga and ^{71}Ga contributed to the NMR signals (the filling factor of the micro-coil was approximately 50 %).

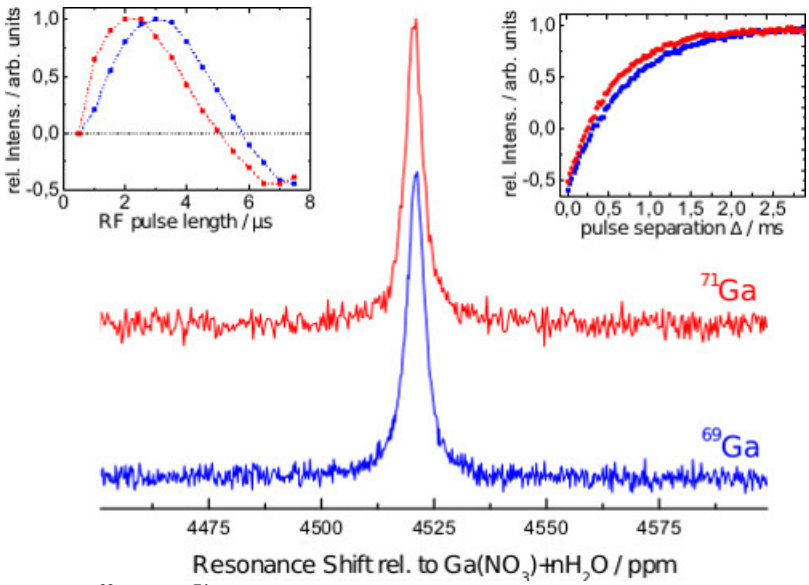
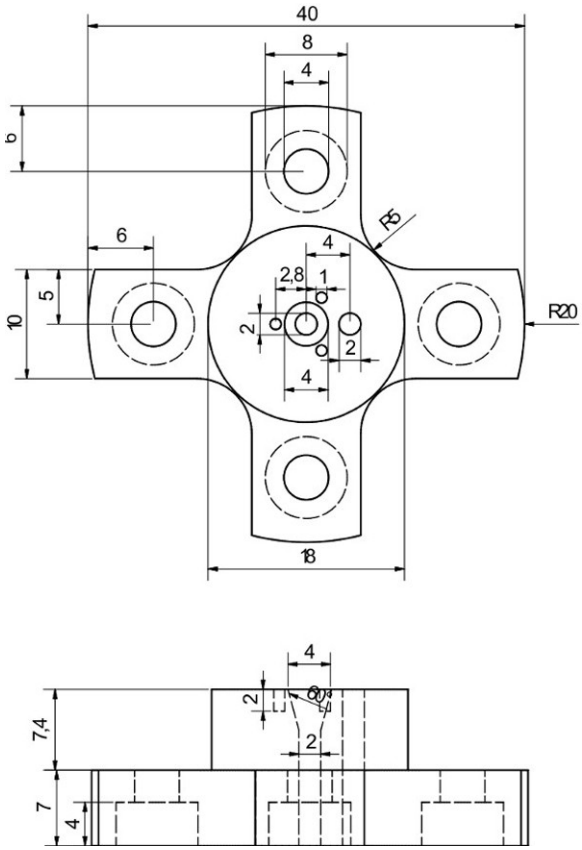
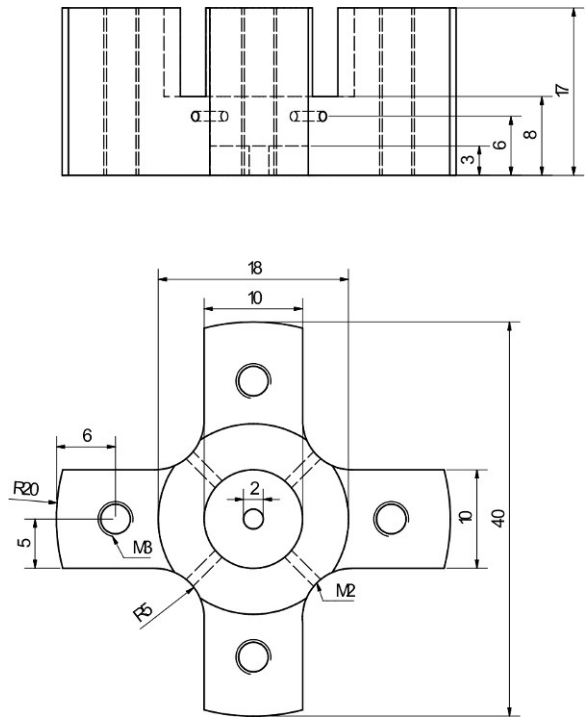


Figure 6. ^{69}Ga and ^{71}Ga NMR of liquid gallium at 1.8 GPa. Recorded NMR spectra of both NMR active gallium nuclei (blue: ^{69}Ga, red: ^{71}Ga) at 1.8 GPa at RT (main frame). The resonance shift was obtained by comparing the signal frequencies with an aqueous $Ga(NO_3)$ solution. Left inset: obtained results from a nutation experiment of both nuclei at 150 mW average pulse power. Right inset: obtained data from a π - π/2 inversion recovery experiment. Please click here to view a larger version of this figure.

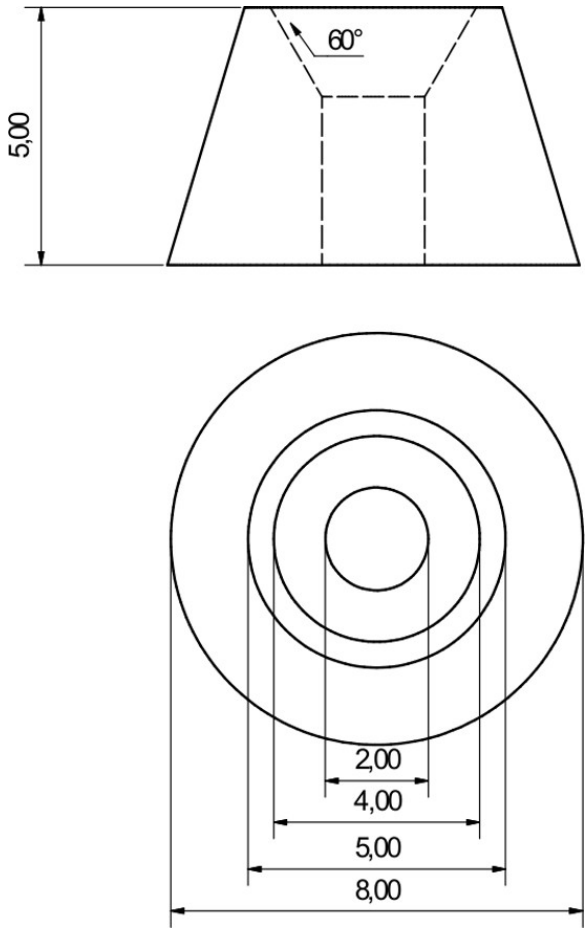
The left inset of **Figure 6** shows a typical result of a nutation experiment with varying pulse length. The right inset of **Figure 6** shows the dependence of the observed signal intensities obtained in a π-π/2 inversion recovery experiment for increasing pulse separation times. Using a single exponential law, the spin-lattice relaxation rates R_1 were determined to $R_1^{69} = 1740\ s^{-1}$ and $R_1^{71} = 2020\ s^{-1}$. All spectra were recorded at a magnetic field of 11.74 T and are accumulations of 500 scans. This leads to a total data acquisition time of only 3 s for a satisfactorily spectrum (the pulse repetition time (RT) was chosen to suffice the relationship: $RT \geq 5/R_1$). A detailed analysis of this data will be given elsewhere.



Supplementary Figure 1. Blueprints of the LAC-TM2 Piston. Please click here to view a larger version of this figure.



Supplementary Figure 2. Blueprints of the LAC-TM2 Shell. Please click here to view a larger version of this figure.



Supplementary Figure 3. Blueprints of the LAC-TM2 XY. Please click here to view a larger version of this figure.

Discussion

A new and promising method to perform NMR at Giga-Pascal pressures was described. This method opens up the door to a broad variety of NMR experiments due to its excellent sensitivity and resolution. Nevertheless, several steps described in the protocol section are crucial to the outcome of the experiment. Especially, the preparation of the micro-coil and its fixation in the Cu-Be gasket is very difficult and requires some experience. In the following, some important tips are given, which should help a first successful application of the technique.

All presented data were obtained using a commercial Apollo or Bruker NMR spectrometers for solid state NMR applications. The magnets were standard wide-bore Bruker magnets with magnetic fields ranging from 7.03 to 17.6 T. Simple home-built NMR probes used for standard NMR experiments were retrofitted to hold the anvil cells.

The cell chassis of the LAC-TM2 should be manufactured according to the blue prints given in the supplementary. Special attention has to be paid to the production of the piston and its corresponding duct in the cell's shell in order to avoid any kind of clearance. Typically, an accuracy of better than 10 µm is desired to ensure a sufficient working stability of the pressure cells under load. A good machine shop can achieve a dimensional accuracy of 0.01 to 0.015 mm. The required M4 Allen countersunk bolts can either be manufactured as well, or purchased from special companies (*e.g.,* see materials list). Throughout the whole cell preparation, use non-magnetic tools since every contamination with ferromagnetic materials will affect the outcome of the experiments. Therefore, use either a titanium scalpel or a glass-writing diamond when carving the channels into the Cu-Be gasket.

For the steps in number 3, several special tools are needed for best results. For preparing the micro-coil, either a set of chuck jaws or a lathe can be used. For the winding of the micro-coil, conical awls can be used (typically in diameters of 180 µm to 450 µm). For sample loading, a piece of wire or a very sharp needle should be employed. It is important to note that the total height of the coil must not exceed the thickness of the gasket's pre-indentation. Typically, micro-coils made of 3 to 5 turns (using an 18 µm copper wire) have a height of less than 100 µm, sufficient for 1,000 µm and 800 µm culet anvils. It is crucial to monitor the DC resistance of the micro-coil at every step following step 3.10. Typically, the expected resistance should be around 1 Ω across the cell, if the resistance breaks down to kΩ or even MΩ, the cell must be opened and the procedure restarted, beginning at step 3.1.

A deformation of the RF micro-coil should be avoided. Empirically, it was found that at pressures above 6 GPa, the Cu-Be gasket starts to flatten with pressure, decreasing the height of the sample hole easily below 50 µm, deforming most micro-coils with more than 4 turns considerably. If anvils with a smaller culet size are to be used in order to reach higher pressures, the resulting sample chamber will be reduced in volume considerably (stemming from the requirements of the gasket design for maximized working stability). For example, by going from a pair of 1 mm to 0.8 mm culet anvils, the sample volume will be reduced from about 10 nl to 3 nl and the number of turns of the micro-coil will decrease from 6 to 4 (if 18 µm copper wire is used). This will typically result in a reduction of the SNR by about one order of magnitude.

At this point we want to stress, that the choice of the gasket material can be crucial. The introduced Cu-Be gaskets may not be suited if pressures above 10 GPa are desired since the above mentioned deformation of the sample cavity will eventually destroy the RF micro-coil. An alternative gasket material may be rhenium, which has a much higher mechanical strength and is non-magnetic. Another established approach was introduced by Boehler *et.al.*[29]where the inner metallic region of the gasket was substituted with a diamond/epoxy mixture;other groups[30] used cubic boron nitride as gasket materials; in order to improve the height to diameter ratio of the sample cavity. This approach was found to be superior to the formerly used metallic gaskets. At this point, the authors gathered some experience with this promising technique which will be published elsewhere.

The threads and bolts of the titanium screws as well as the Allen set keys will wear off after some pressure runs. Therefore, they need to be revised by a machine shop or completely replaced. Choosing the right pressure medium for the experiment is crucial. The pressure calibration, step 4.4, can easily be done using a commercially available optical spectrometer system to observe pressure induced shifts of the R_1 and R_2 lines of the ruby powder. Further information about this well-known technique is given in the literature[31]. The loss of hydrostaticity is indicated by a drastic increase in the line-width of the ruby photoluminescence of the R_1 and R_2 spectra. Best results can be achieved by using liquid nitrogen, liquid noble gases or a 4:1 methanol/ethanol mixture, which are supposed to provide hydrostatic conditions up to pressures in the range of 10 GPa.

The limits of that technique, with respect to standard NMR experiments, lies on the inaccessibility of any magic angle spinning techniques. This drastically limits the resolution to about 5 ppm. On the other hand, NMR measurements on ^{1}H are, at the moment, not recommendable due to the vast variety of spurious proton signals stemming dominantly from the epoxy resin and the polyurethane insulation of the micro-coil as well as the mostly used pressure transmitting medium. Another important point to mention here is that the success of each experiment depend on the samples intrinsic spin relaxation times which sets the length of each acquisition time. Since a fast spectral accumulation is desired in order to reduce the total measurement time, sample with a very long T_1 should be avoided.

It has to be pointed out, that ^{1}H-NMR might not be feasible with our design due to the extensive use of epoxy resins, varnishes, and insulated wire for the micro-coils. Nevertheless, if experiments on protons are desired one needs to by-and-large substitute the 1H containing materials (or use 2H for synthesis where possible).

All other approaches for NMR under high hydrostatic pressures suffered from low SNR and therefore rather long required data acquisition times, which rendered a lot of experiments impossible. The shown micro-coil approach overcomes those obstacles by the coil's dramatically improved filling factor and we have shown that NMR on highly correlated and uncorrelated electron systems is possible.

Finally, we believe that our new anvil cell technique represents a major development in modern condensed matter research. We have shown that this approach enables researchers to perform high sensitivity NMR experiments at pressures up to 10 GPa. First applications prove the power that anvil cell NMR brings to the study of the electronic and chemical structure of modern materials.

Disclosures

The authors have nothing to disclose.

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