



NMR at pressures up to 90 GPa

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ABSTRACT

The past 15 years have seen an astonishing increase in Nuclear Magnetic Resonance (NMR) sensitivity and accessible pressure range in high-pressure NMR experiments, owing to a series of new developments of NMR spectroscopy applied to the diamond anvil cell (DAC). Recently, with the application of electromagnetic lenses, so-called Lenz lenses, in toroidal diamond indenter cells, pressures of up to 72 GPa with NMR spin sensitivities of about 10^{12} spin/Hz^{1/2} has been achieved. Here, we describe the implementation of a refined NMR resonator structure using a pair of double stage Lenz lenses driven by a Helmholtz coil within a standard DAC, allowing to measure sample volumes as small as 100 pL prior to compression. With this set-up, pressures close to 100 GPa could be realised repeatedly, with enhanced spin sensitivities of about 5×10^{11} spin/Hz^{1/2}. The manufacturing and handling of these new NMR-DACs is relatively easy and straightforward, which will allow for further applications in physics, chemistry, or biochemistry.

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1. Introduction

Varying thermodynamic conditions opens the possibility of accessing low-energy configurations, metastable or new states of matter, allowing the investigation of electronic or structural instabilities in solids. Thus, variation of pressure – that is directly reducing atomic or molecular distances – turned out to yield one of the most intriguing branches in condensed matter sciences [1,2].

One of the most popular devices to generate high pressure is the diamond anvil cell (DAC) based on the Bridgman concept of a piston-cylinder press type. It was first introduced in the mid-fifties [3], and uses two diamond anvils to push together and compress a sample placed between their flattened faces. Since these first pioneering works many developments have been implemented such as the introduction of gaskets to confine the sample, pressure scale, pressure transmitting medium, laser heating. For the past two decades, it has now become a near routine to generate high pressure of 100 GPa in the laboratory, even reaching pressure found at the centre of the Earth [4,5] and beyond [6,7]. The success of the diamond anvil cells (DACs) resides in its astonishing variability in both design and field of application. To this end, *in-situ* spectroscopic methods in DACs are established, exploiting the diamonds' transparency to a broad range of wavelengths using

lasers or X-ray spectroscopy techniques covering most of the available pressure range. Other spectroscopic methods such as NMR or EPR, however, appear to be almost impossible to implement in DACs due to the following reasons: (i) Sample cavities in DACs are typically tightly surrounded by both diamonds and a hard, metallic disc serving as a gasket. The gasket prevents the sample from leaving the region of the highest pressures, and provides so-called “massive support” to the stressed diamond anvils [8]. (ii) Due to the necessarily small dimensions of the diamond anvils, available sample space is often much less than 5 nL before compression, which is further reduced when pressures exceeding several GPa are targeted. An application above 40 GPa, for example, requires an initial sample cavity of about 100 μm diameter and about 40 μm in height, amounting to about 350 pL. (iii) Finally, the sample cavity is prone to plastic deformation under compression, leading to a volume reduction of the cavity of up to 50% within a rather small pressure range, depending on the choice of gasket material and pressure medium [9].

Thus, a successful implementation of NMR – or pulsed ESR for that matter – in diamond anvil cells, requires the implementation of resonators with suitable sizes and design. The first attempts have employed complex coil arrangements, either placed on the diamonds pavilion or over the whole diamond assembly, but did not allow measurements for pressures above 3–5 GPa [10]. A more promising solution has been the implementation of RF micro-coils directly into the high pressure sample chamber with

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measurements reaching pressures of up to 8 GPa [11,12] and maximal pressures as high as 20–30 GPa [13,14]. However, these minuscule micro-coils are extremely sensitive to the plastic deformation of the sample cavity, often exhibiting significant losses of B_1 field strength and subsequently NMR sensitivity by almost two orders of magnitude within a single pressure run [15,16].

Recently, the application of electro-magnetic Lenz lenses in toroidal diamond indenter cells demonstrated that NMR at significantly higher pressures is not only feasible, but also comparatively easy to implement [17]. The basic principle of these magnetic flux tailoring devices is governed by Lenz's law of induction, hence the name Lenz lens (LL). A LL is, in the most general terms, a flux transformer with its outer winding collecting the magnetic flux generated by an often somewhat larger excitation coil. The r.f. current built up within a thin perimeter of the LL will lead to a deposition of the magnetic flux in the geometrically pre-defined inner area.

Resonators using such LLs are typically driven by a bigger excitation coil directly connected to the NMR spectrometer. Following an RF pulse into the driving coil, the LL picks up the RF field via mutual inductance. The induced RF current is built up in the outer winding of the LL resonator and deposited in an inner region via a counter-winding, leading to a significant amplification of B_1 in a pre-defined volume. This basic idea of course makes LL resonators in DACs very attractive, as they can be used to focus the RF B_1 field where the high-pressure sample is located.

However, the latest design introduced by Meier et al. displayed some drawbacks. Its application in a DAC requires two diamond anvils with different culet diameter with, typically an 800 μm culet diamond on the cylinder side facing a 250 μm culet diamond on the piston side exerting the actual force. The main advantage of this technique is that the metallic rhenium gasket is buckled towards the much sharper piston anvil, leaving the space close to the 800 μm mostly untouched. This leaves enough room to place the RF excitation coil on the pavilion of the base anvil close to the culet, and thus to the 600 μm outer diameter LL used in these experiments. However, such anvil arrangements limit the accessible pressure range [18], with anvils damaged at a much smaller pressure range, often 60% below the standard capabilities of DAC experiments. Here, we introduce a new design and fabrication of RF resonators allowing for a further increase in maximal pressures and NMR sensitivity.

2. Structure and preparation of the DSLL-resonator

Fig. 1 shows the principle design idea of the double-stage LL (DSLL) resonator.

The pressure cells equipped with these resonators were prepared as follows: After careful alignment of two 250 μm culet diamond anvils, a 250 μm thick rhenium disc was pre-indented to ~ 20 μm thickness. A ~ 80 μm sample hole was cut in the centre of the pre-indentation using an automated laser-drilling system at the Bavarian Geoinstitute (BGI).

PVD (Physical Vapor Deposition) coating of the diamonds has been performed using a Dreva Arc 400 (manufacturer: VTD). An ultrapure copper target from Chempur (99.999%) has been used. Argon (0.01 mbar) served as processing gas for plasma sputtering. The power of the Pinnacle magnetron power supply was set at 300 W. In order to achieve the required thickness of the copper layer (~ 2 μm) the duration of the coating process was set to 20 min. Using a focused ion beam (Scios Dual beam from FEI), the shape of the DSLL resonator was cut out from the almost homogeneous copper layer, using a 30 kV beam accelerator voltage and 65 nA gallium ion beam current.

Fig. 2 shows SEM images during the DSLL resonator preparation on one of the diamond anvils. Additionally, the rhenium

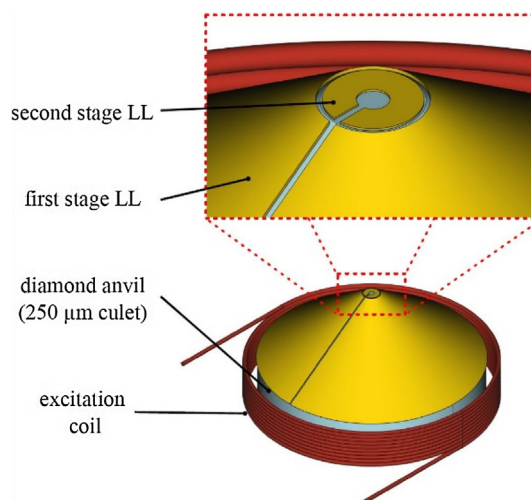


Fig. 1. Schematic design of the double stage Lenz lens (DSLL) resonator. Only one half of the complete assembly is shown. Both first and second stage LL are made from a 1 to 2 μm thick layer of copper deposited using PVD and cut into the depicted shape using a FIB. The driving coil, an 8-turn coil made from 100 μm copper wire is placed around the diamond anvil on the metallic anvil support (not shown). For further details, see text.

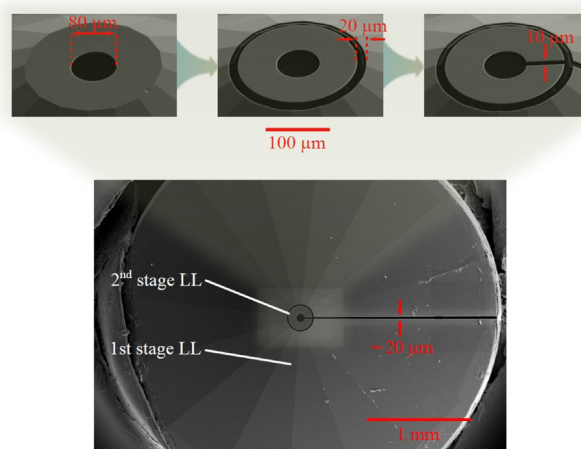


Fig. 2. Representative SEM images of the DSLL resonator structure. The complete anvil can be seen on the left, incorporating both 1st and 2nd stage Lenz lenses. The slit in the 1st stage LL on the anvils pavilion is about 15 μm at its smallest point and increases a bit due to divergence of the gallium ion beam during cutting. The close up (right) shows the 2nd stage LL in detail. Bright spots on both photos are due to small dirt particles.

gaskets were covered with a 1 μm layer of Al_2O_3 on both sides providing electrical insulation between the lenses and the metallic gasket.

The excitation coils were prepared from 100 μm PTFE insulated copper wire and consisted of 8 turns with a diameter of 4 mm. Both coils were placed on the backing plates of the diamonds, fully enclosing the anvils. Subsequently, the prepared anvils were aligned again in the DACs, and the cells were loaded with distilled water and slightly closed to prevent water leakage.

After the cells were closed, both coils were connected in order to form a Helmholtz arrangement. The loaded and pressurised cells were then mounted on a home built NMR probe for standard wide-bore magnets. Analysing the return-loss spectrum of the resonator at 400 MHz, a quality factor of the resonance circuit of about 40 was found.

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