AIP Review of Scientific Instruments

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Citation: Rev. Sci. Instrum. **77**, 073905 (2006); doi: 10.1063/1.2221537
View online: http://dx.doi.org/10.1063/1.2221537
View Table of Contents: http://rsi.aip.org/resource/1/RSINAK/v77/i7
Published by the American Institute of Physics.

Long symmetric high-pressure cell for magnetic measurements in superconducting quantum interference device magnetometer

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(Received 16 May 2006; accepted 17 June 2006; published online 19 July 2006)

We describe a high-pressure cell for magnetic measurements in a magnetic property measurement system superconducting quantum interference device (SQUID) magnetometer. The cell has been developed for studies of weakly magnetic materials and has the operating pressure limit of 1 GPa. Its design is focused on reducing the background signal by making the pressure cell symmetric with respect to the sample in order to provide an integrable SQUID response. The use of an externally loaded cylinder has resulted in the increased strength of the cell and in the provision of a larger sample volume. The optimization of the cell's length has made it possible to use the approximation of an infinitely long cylinder in the whole range of accessible pressures and to apply the Lamé equation for calculating the change in the diameter of the cell as a function of applied pressure. This enabled us to remove a superconductive manometer from the cell and use the diameter-pressure calibration instead. This has further increased the sensitivity of the measurements at low temperatures which is particularly relevant to studies of weakly magnetic materials. The performance of the cell is illustrated by the results of high-pressure measurements on the molecular antiferromagnet $[N(C_2H_5)_4][FeCl_4]$. © *2006 American Institute of Physics.*
[DOI: 10.1063/1.2221537]

I. INTRODUCTION

The application of pressure to materials provides a powerful method of tuning various physical properties, with the potential to induce new functionality, and new insights into their fundamental behavior. While this approach has been extensively exploited in fields such as superconductivity, it is perhaps underutilized in solid-state magnetism. One reason for this is the current limitations in the instrumentation necessary to subject a wide range of materials to pressure while studying the magnetic response. In particular, there is a need to improve pressure cells for use with magnetometers and susceptometers, of which the superconducting quantum interference device (SQUID) magnetometer is probably the most widely used, sensitive instrument for such work.

The magnetic property measurement system (MPMS®) from Quantum Design (USA) (Ref. 1) is probably the most advanced, user friendly and, therefore, the most popular SQUID magnetometer in the world. The MPMS can resolve magnetic moment changes as small as 10^{-8} emu over a wide range of temperatures and magnetic fields. There has long been a desire among the research community studying magnetic properties of materials to add pressure as a variable for the measurements in the MPMS. However, the MPMS puts severe constraints on the design of the pressure cell. The major constraint is one of size as the diameter of the inner bore of the MPMS is only 9 mm. This limits the design option to the piston-cylinder type of pressure cell. Several pressure cells of this type utilizing different design concepts have been made for the MPMS.[2–8]

The aim of this work was to design a high pressure cell for the MPMS which could be used for measuring the susceptibility of weakly magnetic materials. For example, molecular magnetic materials are highly compressible and their properties can be radically modified by the application of even modest pressure (see, for example, Ref. 9). However, such studies have been almost entirely limited to materials that show spontaneous magnetization and hence a strong signal at low temperatures. A cell with greater sensitivity would open up the high-pressure study of a much wider range of molecular magnetic materials including low-dimensional antiferromagnetic systems and magnetically dilute organometallic materials.

II. EXISTING PRESSURE CELLS FOR MPMS MAGNETOMETERS

In this section we will review the existing high-pressure cells for MPMS magnetometers all of which are of piston-cylinder type. The first reports on high-pressure cells for the MPMS appeared in 1996.[2,3] A short high-pressure cell made of a titanium alloy was developed by Reich and Godin.[2] The body of the cell is a short cylinder opened from one end. The

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cell had a pressure limit of 0.5 GPa and the pressure is measured using the superconducting transition in lead.

The cell developed by Diederichs *et al.* has a more advanced design.[3] The body of the cell is a long cylinder made of CuBe alloy and the cell is capable of achieving pressures of 1 GPa. An interesting feature of this pressure cell is the use of the change in the length of the cell as an alternative to using a superconducting transition in lead for measuring applied pressure. The sample inside the cell is surrounded by quartz spacers which have a dual function. They (i) keep the sample separated from the ends of the cell providing a more symmetric distribution of the background signal and (ii) shorten the path of the piston by displacing the pressure transmitting liquid. However, the magnetic signal of the quartz spacers contributes to the background of the cell and should be corrected. The pressure in this cell is created by applying the load in a hydraulic press.

There are several pressure cells based on the design mentioned above. Uwatoko *et al.* used a similar cell in their studies of $YbInCu_4$.[4] Kamishima *et al.* has developed another version of this cell.[5] It was made of titanium alloy and the sample was locked in a polytetrafluoroethylene (PTFE) capsule along with the pressure transmitting fluid, providing quasihydrostatic conditions for the sample. A speck of Sn was also loaded into the cell to measure the pressure by its superconducting transition.

Kamarád *et al.* have built a short CuBe pressure cell in which the sample is attached to the plug holder and the lead pressure sensor rests on the piston at the opposite end.[6] However, the advantage of this cell (in our view) is the use of a screw instead of an external press for driving the piston and applying the pressure, thus providing convenience and simplicity of use.

There is also a commercially available pressure cell for the MPMS manufactured by easyLab Technologies, called the Mcell 10.[7] This is a short pressure cell with the sample, pressure manometer and the pressure transmitting fluid contained in the PTFE capsule, similar to the design used by Kamishima *et al.*[5] The pressure is created by the use of a specially designed hydraulic oil press ram.

All of the pressure cells mentioned above apart from the early one developed by Reich and Godin[2] are capable of achieving pressures of about 1 GPa. There has been a recent report by Uwatoko *et al.* on a very short piston-cylinder cell capable of reaching pressures of 2.0 GPa.[8] The body of the cell is made of hardened CuBe alloy with pistons made of ZrO_2 and the sample arrangement is similar to what Kamishima *et al.* have used.[5]

III. HIGH-PRESSURE CELL DESIGN

Having reviewed all of the existing cells we have not found one that would fully satisfy our experimental requirements. We need a cell that would be suitable for high-pressure studies of magnetic samples with low magnetic susceptibility at the lowest temperatures achievable in the MPMS. This results in several constraints being imposed on the design.

A. Challenges and design solutions

First, the background of the sample support and the cell itself should be symmetric with respect to the sample, so that the SQUID signal from the sample inside the pressure cell would be integrable by the standard MPMS MultiVu™ software.[1] This means that the body of the pressure cell should be a cylinder long enough to provide sufficient clearance between the sample and the pistons even at the maximum pressure. In the MPMS such a distance would be 20 mm, which corresponds to the typical dc scan length of 40 mm.

Second, the volume available to the sample should be as large as possible in order to maximize the sample's contribution to the overall signal detected by the SQUID element. For the dc scan over 40 mm the length of the sample should not exceed about 10 mm. Further increase in the sample volume can thus be achieved through an increase in the diameter of the sample space.

Third, pressure should be measured by means other than the use of manometers such as Pb, Sn, or In with known pressure dependence of the superconductive transition.[10,11] An alternative method for measuring the pressure change is through the change in the external dimensions of the cell. The most sensitive method would involve the use of strain gauges.[12] However, they would have to be glued to the surface of the pressure cell near the sample position and would contribute to the background. Therefore, optical or mechanical micrometry should be used to measure the changes in the dimensions of the cell.

Fourth, the pressure acting on the sample should be fully hydrostatic, i.e., the use of PTFE capsules should be avoided. And finally, the pressure inside the cell should be induced by means of screws rather than with the use of external press. From our experience it can be difficult to keep such a long pressure cell well aligned in the press during pressure application and a slight misalignment can lead to the piston being jammed inside the cell. On the other hand, the use of a dedicated press (such as the one used in the Mcell 10 design[7]) would add to the cost of making the cell.

B. Calculations and finite element analysis

Prior to developing the detailed design of the cell we have made some estimates of the dimensions involved. Since one of the requirements for the pressure cell was to be able to measure the pressure inside by the distortion of the outer dimensions of the cell, we have used the Lamé equation to see if the change in the outer diameter of the cell with pressure will be sufficient to be used for accurately measuring the pressure inside.[13] The chosen outer diameter of the pressure cell of 8.7 mm is limited by the bore diameter of the MPMS sample chamber, which is just 9.0 mm. In order to maximize the sample volume we have chosen the largest inner diameter of all of the reviewed pressure cells, i.e., 3.0 mm. Using the Eq. (A3) and for the chosen values of $a=1.5$ mm and $b=4.35$ mm, $E=125$ GPa, and $\mu=0.285$ (see the Appendix), we have calculated that the change of the diameter of the cell with pressure is $dD/dP=16$ μm/GPa and, therefore, would

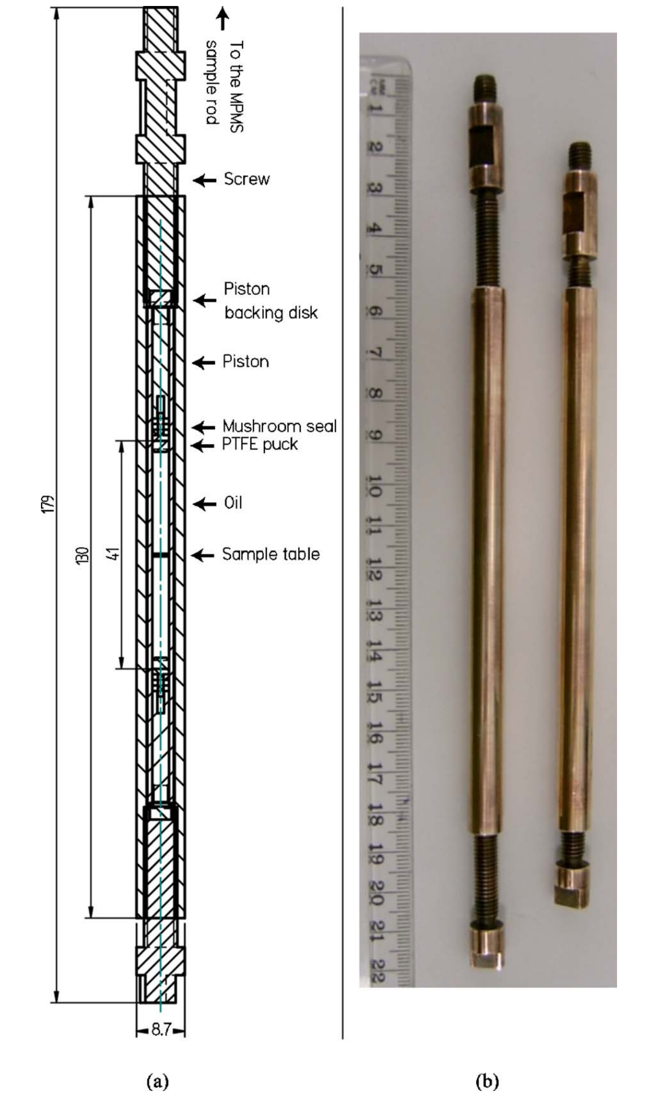

FIG. 1. (a) Drawing of the cell with the distance between the pistons shown for the top applied pressure and (b) photograph of the high-pressure cell at ambient pressure (left) and at top pressure (right).

be measurable with a standard digital micrometer with a resolution of 1 μm.

However, the Lamé equation has been developed for the case of an infinitely long cylinder. In order to check the validity of the long-cylinder approach we have applied finite element analysis to our design of the pressure cell using the ANSYS® software package.[14] The analysis has confirmed that even for the smallest sample volume, corresponding to the maximum applied pressure, the Lamé equation holds and the diameter of the cell is a linear function of the applied pressure.

C. High-pressure cell

The design of the pressure cell is shown in Fig. 1(a). All parts of the cell are made of BERYLCO-25 alloy.[15] The body of the cell consists of two coaxial cylinders with interference fit for extra strength. Because the parallelism of the bore and the surface finish are important for successful operation of the cell, all internal and external surfaces of the two cylinders have been honed and the cylinders were assembled by shrink fitting. The outer surfaces of the pistons are also honed to achieve the best possible fit between the piston and the cylinder.

Below we describe the procedure for assembling the cell. In the first instance one of the pistons with a mushroom seal with tin and copper washers is positioned inside the bore in such a way that the mushroom assembly just enters the bore of the cell. The piston is then backed up with a backing disk and the screw. In order to expand the tin and engage the seal we gently press on the mushroom assembly with a rod through the opposite end of the cell. Then we fill the cell with pressure transmitting oil just above the midpoint of the bore and insert the sample. We used Daphne 7373 oil as a pressure transmitting medium.[16]

The sample is mounted on a clover-shaped puck made of PTFE or gelatine with a diameter slightly larger than the inner diameter of the cell. The sample is sized in such a way that its diameter is somewhat smaller than the bore of the cell (a powder sample needs to be pressed into a pellet prior to mounting), so that the pressure transmitting liquid could flow freely around it without moving the sample puck from its position. The puck with the sample is then inserted into the cell and positioned in the center of the cylinder. The cell is then filled with oil almost to the top of the bore and the oil is stirred with a wire rod in order to get rid of any air bubbles trapped inside. At this stage the second piston assembly can be inserted; however, we have found that for the mushroom to provide a good seal during the initial compression the tin should be expanded just as in the case of the first piston. With the other end already closed it is impossible to push on this mushroom with a rod. To overcome this problem we use a short tapered PTFE puck with the diameter marginally larger than the diameter of the inner bore of the cylinder. Once pushed inside the bore it provides sufficient initial pressure on the mushroom to expand the soft metal seal. In order to provide fully symmetric environment for the sample we now also insert such a PTFE puck when we assemble the first piston [Fig. 1(a)].

The cell is now at ambient pressure and is fully symmetric with respect to the sample. In order to keep it this way at all pressures the operator just needs to make sure that the top and the bottom screws that drive pistons towards each other are rotated the same number of turns. The length of the cell at ambient pressure (i.e., with the pistons all the way out) is such that it utilizes the whole available space inside the MPMS sample loading chamber. As the pressure is increased the overall length of the cell decreases [Fig. 1(b)]. Once the required pressure is achieved the pressure cell is attached to the standard sample rod by means of an M6 $\times$ 1 thread on the top screw and a simple two-way threaded adapter.

D. Pressure calibration and compressibility of Daphne 7373 oil

In order to establish the actual dependence of the diameter of the cell on the applied pressure we have conducted an experiment, in which a sample of lead has been loaded into the pressure cell. The pressure was applied in steps at which the diameter of the cell expanded in increments of 1 μm as measured by a digital micrometer. The cell was then placed

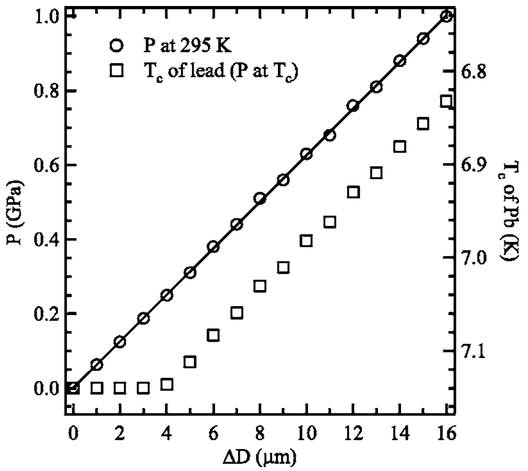

FIG. 2. Squares indicate the temperature T_c of the superconductive transition in lead (right axis) and the corresponding pressure at T_c (left axis) as a function of the change in diameter of the pressure cell ΔD measured at room temperature. Circles show the corresponding pressure at $T=295$ K (left axis) as a function of the change in diameter of the pressure cell measured at room temperature vs ΔD. The solid line is the linear fit to the data.

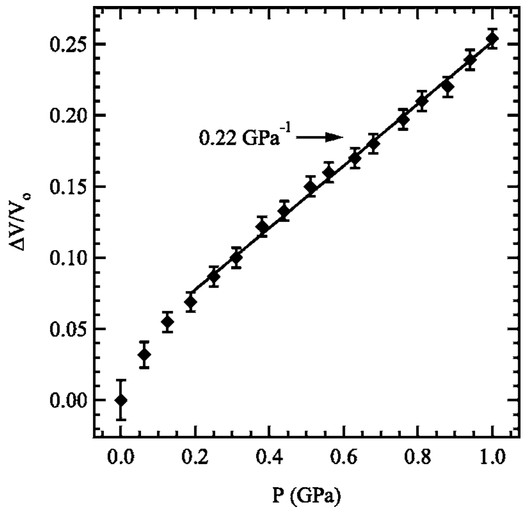

FIG. 3. Compressibility of Daphne 7373 oil. The solid line is a linear fit above 0.2 GPa.

inside the MPMS sample chamber and the temperature T_c of the superconducting transition in Pb was measured using the standard procedure.[2,6] The results of this experiment are presented in Fig. 2.

The pressure at the superconductive transition T_c of lead was calculated by its known pressure dependence $dT_c/dP=0.405$ K/GPa.[17] Because of the difference in thermal expansion coefficients of the CuBe alloy and the oil used as a pressure transmitting fluid, the pressure drops as the pressure cell is cooled down. This explains why the first nonzero pressure point appears in the T_c data at $\Delta D \approx 4$ μm (Fig. 2). However, it is clear that when the pressure is completely released at room temperature, it will remain zero when the pressure cell is cooled down. This zero reference point combined with the linear dependence of $T_c(\Delta D)$ allows us to work out how the diameter of the cell changes with pressure at room temperature. This can be achieved by shifting all of the high-pressure low-temperature data points, except the zero point, so that they form a continuous straight line with the point at $P=0$ GPa (circles in Fig. 2). The required offset representing the pressure drop inside the cell as it is cooled from 295 to 7 K is 0.24 GPa. This value is very similar to the number reported for Daphne 7373 oil.[6]

A linear fit to the room temperature data in Fig. 2 shows that $dP/dD=0.062$ GPa/μm or that the diameter of the cell changes with pressure as $dD/dP=16$ μm/GPa, which is exactly the number predicted by the Lamé equation. Thus the data presented in Fig. 2 show that the change in the diameter of the cell can be used as a sensitive indicator of the applied pressure. This not only eliminates the need to measure the superconductive transition at low pressure but also allows the operator of the cell to know what pressure is applied, in advance of the measurement, and also to spot an oil leak early if it occurs.

As we were calibrating the diameter of the cell as a function of pressure, we have also measured the compressibility of Daphne oil. Simple piston-cylinder design of the cell allowed us to extract the volume of the oil inside the cell by monitoring the position of the two screws during the loading. The relative volume change as a function of presure at $T=295$ K is presented in Fig. 3.

Daphne oil is quickly gaining popularity among the high-pressure community[5,6,8,16] and we believe these data will be useful to users and designers of high pressure equipment as they provide direct information on the pressure-volume relationship for this pressure transmitting medium.

IV. HIGH-PRESSURE MEASUREMENTS ON A MOLECULAR ANTIFERROMAGNET

Our main motivation was to build a pressure cell suitable for studies of weakly magnetic materials with critical temperatures lower than the temperature of the superconductive transition in pressure standards such as Pb ($T_c=7.20$ K), Sn ($T_c=3.73$ K), or In ($T_c=3.40$ K).[11] Such a pressure sensor when placed inside the cell contributes significantly into the background when in the superconductive state.

One of the systems which falls into the category of materials described above is the tetraethylammonium tetrachloroferrate $[N(C_2H_5)_4][FeCl_4]$. At ambient pressure, it has a transition into an antiferromagnetic (AF) phase at $T_N=3.0$ K.[18] It has been studied as a model one-dimensional (1D) system since 1960s, but its magnetic properties have never been studied at high pressure until now. The results of this study are discussed in detail elsewhere;[19] here we would like to focus on the quality of the data obtained in the pressure cell.

The measurements were performed on a polycrystalline sample with the weight of 20.7 mg. The temperature dependence of the dc magnetic susceptibility at different pressures is presented in Fig. 4.

The effect of pressure on the Néel temperature is apparent from the inset in Fig. 4 as T_N increases with applied pressure at the rate of 2.0 K/GPa. The solid line corresponds to the data collected on the same sample in a standard MPMS environment, i.e., in a gelatine capsule inside the

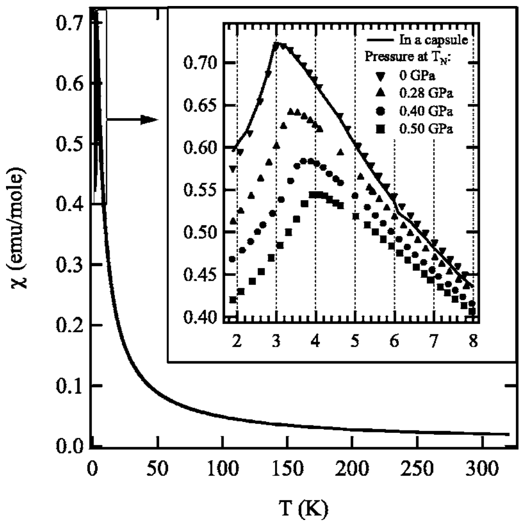

FIG. 4. Magnetic susceptibility of $[N(C_2H_5)_4][FeCl_4]$ as a function of pressure. The inset is the zoom into the low-temperature region with the solid line showing the data collected on the sample in a standard MPMS gelatine capsule and the straw.

plastic straw. As can be seen from the inset these data are almost a perfect fit to the data collected inside the pressure cell at zero pressure.

The high-pressure data in Fig. 4 are presented in the form uncorrected for the background. We have found that the background correction needs to be applied if the signal is lower than 10^{-5} emu. However, because the pressure cell is fully symmetric with respect to the sample position, the SQUID response remains symmetric and, therefore, integrable down to 10^{-7} emu. This simplifies the task of applying the background correction and makes the measurements possible on samples with low magnetic susceptibility.[20,21]

ACKNOWLEDGMENTS

The authors wish to acknowledge useful discussion with J. Kamarád on mechanical properties of CuBe alloy and on the properties of Daphne 7373 oil as pressure-transmitting medium. This work was supported by EPSRC Grant No. EP/D503744/1. One of the authors (S.T.) also thank the Royal Thai Government for a studentship.

APPENDIX

From Eq. (44) of Ref. 13 it follows that the radial displacement u of a cylinder loaded in the axial direction is

$$u = \frac{1-2\mu}{E}\frac{P_a a^2 - P_b b^2}{b^2 - a^2} r + \frac{1+\mu}{E}\frac{a^2 b^2}{r}\frac{P_a - P_b}{b^2 - a^2}, \qquad \text{(A1)}$$

where μ is Poisson's ratio, E is Young's modulus, r is radial elongation, a and b are internal and external radii of the cylinder, respectively, and P_a and P_b are internal and external pressures acting on the cylinder, respectively.

For an internally loaded cylinder $P_a = P$ and $P_b = 0$. Then the radial displacement of the outer surface of the cylinder becomes

$$u\big|_{r=b} = \frac{Pb(2-\mu)}{E(b^2/a^2 - 1)}. \qquad \text{(A2)}$$

So, the change in the outer diameter of the cylinder D ($D = 2b$) with internal pressure P is

$$\frac{dD}{dP} = \frac{2b(2-\mu)}{E(b^2/a^2 - 1)}. \qquad \text{(A3)}$$

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