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Abstract

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Reference

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Multiprobe experiments under high pressure: Resistivity, magnetic susceptibility, heat capacity, and thermopower measurements around 5 GPa

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We have performed multiprobe experiments using a Bridgman-anvil pressure cell, adapted to trap Daphne oil as pressure medium. Resistivity, ac-magnetic susceptibility, thermopower, and ac-heat capacity of a type-I superconductor, lead, have been studied at low temperature up to 5 ± 0.1 GPa. This is the first report where ac-magnetic susceptibility has been measured in this type of pressure cell and at such a high pressure range. The signature of the superconducting transition temperature, obtained from all these different measurements, agrees well within the experimental errors. © 2010 American Institute of Physics. [doi:10.1063/1.3360819]

I. INTRODUCTION

High pressure (p) is one of the most important tuning parameters in modern experimental condensed matter physics. Over the past few decades tremendous progress has been observed in this field. Different techniques under pressure have been developed to investigate electronic transports, various spectroscopies (x-ray, neutrons, NMR, and Mößbauer), and many other magnetic and thermodynamic properties. In order to obtain complete and coherent information, sometimes it is necessary to investigate multiple properties of a system. Concerning high pressure experiments, measurement data obtained in different pressure cells is not always easy to exploit. This is partly because the systematic errors and the pressure homogeneity vary from cell to cell. In most of the cases it is difficult to apply a similar pressure inside different setups and being a destructive method of measurement, a sample is, usually, not suitable after one experiment. Moreover, it requires a considerable time to realize and perform individual experiments separately. A multiprobe experiment is an elegant solution to overcome these difficulties. In such an experiment, different physical properties are measured on a single sample and in one pressure cell. The price one has to pay is the need to take into account of different constraints of several setups, which means a higher degree of complexity and that the ideal conditions for a single property may not be completely achieved. Some of the past examples of multiprobe experiments, under pressure, are in situ x-ray diffraction and electrical resistance measurements, calorimetric, and transport investigations and more recently, electronic, and magnetothermal transport measurements. Here, we report the setup and results of a multiprobe experiment using a single Bridgman-anvil pressure cell and a liquid medium. The developed setup provides to study four properties: resistivity (ρ), thermopower (S), ac-heat capacity (Cac), and ac-magnetic susceptibility (χac) under high pressure. It has the unique design that both the primary and the secondary coils are inside the pressure cell. At this initial stage of the development, lead (Pb) is used to calibrate this setup up to a pressure of about 5 GPa.

II. EXPERIMENTAL SETUP

The experiment is performed in a modified Bridgman-anvil cell, recently developed in our group by Rüetschi et al. to use liquid as pressure medium. The pressure transmitting medium is Daphne oil 7373 from Idemitsu Kosan Co., Ltd., Japan. Anvils made of nonmagnetic tungsten carbide (WC) with a angle of 6° are used. The anvils, whose flat part has an overall diameter of 3.5 mm, are press-fitted in copper-beryllium (Beryco 25, CuBe) shrink collars. One of the most advantages of Bridgman-anvil cells is their wide pressure range and a large number of wires can be introduced into the pressure chamber. This is particularly important in a multiprobe experiments where one needs to introduce a large number of wires. The sample space is formed by a pyrophyllite gasket which is squeezed between the flat part of two opposed anvils. Pyrophyllite, an aluminum silicate hydroxide, was chosen as the gasket material because its friction coefficient with respect to metal is quite high. High frictional forces allow the gasket to withstand the high pressure difference existing across its width. Since pyrophyllite is a porous material, one needs to take some special care while dealing with liquid pressure medium. Better results are achieved when the inside of the gasket is covered with an epoxy film, which prevents any absorption of the liquid medium. There is no such problem at high pressure because the gasket becomes water-proof as pyrophyllite undergoes a plastic transformation. The photo of the pressure cell is shown in Fig. 1; the picture was taken at ambient condition before applying any load. The setup is directly built on the bottom anvil. The gasket consists of two almost identical pyrophyllite rings with a total height of about 0.194 mm. The proper gasket height is realized after a series of attempts with test cells in order to ensure a stable gasket. The outer diameter is ad-
justed to the flat part of the anvil, while the inner diameter is about 2 mm. One of these rings with a height of about 0.097 mm is glued on the anvil with a sodium silicate solution and in addition fixed on the outside with epoxy (fast hardening araldite). For detail description about the wire passage through the gasket, interested readers are again encouraged to see our previous work.\textsuperscript{1} The electrical contacts between the outer and inner wires establish in the gasket when the cell is pressurized. In order to have a contact at ambient pressure a droplet of silver paste is added just outside the gasket. To reduce the mechanical force on the sample contacts during pressurization, supports (R’s in the Fig. 1) are placed in the cell between the sample and the pyrophylite gasket on which the wires are stuck. The second pyrophylite ring is placed on top of the first one and fixed on the outside with epoxy. Partially polymerized epoxy is used to prevent flowing by capillarity into the wire passages and in between the two gasket rings. The inside of the gasket is sealed with an epoxy film of about 40 μm thickness. Here, again, partially polymerized epoxy is used to prevent the flow over the anvil. The upside of the gasket is coated with the sodium silicate solution. The clamp is of hollow cylindrical shape, made of a nonmagnetic titanium-aluminum-vanadium alloy (Ti-6Al-4V, ASTM F136). Both ends can be closed by screws. For pressurization, the clamp is suspended in a support. The load is applied by the piston of an oil press passing through a hole in the upper screw. The wires can leave the clamp through four windows which are located at the height of the anvils. They are then moved to the lower end of the clam through trenches. A separate copper jacket is used for thermalizing the clamp, particularly at very low temperature (T). Two of the windows which are not used for the wire passage can be filled with copper pieces. The copper jacket presses these pieces against the shrink collars which are in good thermal contact with the anvils. The electrical leads also help to thermalize the sample. The thermometer, a Cernox resistor, is placed inside a small copper block which is fixed in the jacket.

High purity (99.99+%) lead is chosen as sample because it can be easily shaped and serve as an indirect manometer. The thickness of the sample is 21 μm, obtained by rolling, while the width of 41 μm is carefully cut using a razor blade. The total length of the sample is 0.864 mm. All the contacts are established out side of the pressure cell. Air annealed 4N purity gold wires with a diameter of 10 μm are used to form contacts on the sample. First, the leads of Au and AuFe (0.07%Fe) near the sample heater H are spot-welded in front of each other and at about 20 μm inside the sample width as shown in Fig. 1(b). They serve as thermocouple and are also used as current and voltage leads for the resistance measurement. Then the sample is introduced inside two concentric coils, made of insulated copper wire with a diameter of 13 μm (supplied by Goodfellow Inc.). After that, two gold wires are spot-welded on the other free end of the sample. The coils are prepared using a special tool which can be manipulated by hand under a stereoscopic binocular (magnification up to 100 times). This tool holds a small tungsten rod with a diameter of 50 μm, which is the inner diameter of the secondary coil. A coil is formed by winding up the wire around the tungsten rod. First, the secondary is coiled up to 43 turns, and then an extremely thin layer of prepolymerized epoxy is added. Prepolymerization of the epoxy is necessary in order to prevent the coil from being glued on the tungsten support. We coiled the primary in a similar way and with the same number of turns. The external diameter of the primary is 100 μm, which is about two third of the total height of the pressure chamber and length of both coils is 0.6 mm. The filling factor \( \frac{V_s}{V_v} \), which is defined as the ratio between the sample volume \( V_s \) to the volume inside the secondary coil \( V_v \), is 0.43. The moderately low value is due to the rectangular cross-section of the sample. In most of the previous measurements, the primary coil is generally located outside of the anvils. But in the present case, the design of the ac-susceptibility setup is quite unique: for the first time, we have placed both the primary and the secondary coil inside a pressure cell. The design has the advantage that it provides a better reduction of the background, e.g., parasitic signals which may appear from the environment of the pressure cell. Two separate, continuous, shielded brass wires (supplied by Cambridge Magnetic Refrigeration) are used for the excitation and the detection of the signals from the coils. A more detailed description regarding the ac-magnetization measurement will be discussed later. As heater (H) we have used a flattened constantan wire of 12 μm in diameter and two gold wires are spot-welded at the extremities. The heater has a resistance of 1 Ω and it is used to measure ther-

FIG. 1. (Color online) Setup for the multiprobe experiment on Pb. P1 and P2 indicate terminals of the primary coil. S1 and S2 are those of the secondary and H is the sample heater. (b) Expanded view of the marked rectangle in (a) shows the setup near the heater and the thermocouple junction. R indicates two of the various supports, below a wire, made of small pieces of copper.
mopower and ac-heat capacity. The sample is electrically insulated from the heater by depositing a thin insulating layer of varnish on both the sample and the heater. The heater is glued to its support and before completed polymerization it is pushed to the extremity of the sample. Finally, a drop of epoxy is added in the junction between the sample and the heater, as well as the thermocouple wires and the heater extremities to ensure a better thermalization. All the wires coming out from the pressure cell are connected to low impedance copper wire up to 300 K. The Keithley 224 programmable current source is used and the voltage is measured by a dc nanovoltmeter (EM, model A14). For heating the temperature of the sample above 4.2 K, a heater with resistance 22 Ω is mounted near the clamp of the cell.

### III. RESULTS AND DISCUSSIONS

An exemplary result of this multiprobe experiment is shown in Fig. 2. Resistivity, ac-magnetic susceptibility, ac-heat capacity, and thermopower measurements are displayed at a pressure of 4.1 GPa. The onset of the SC transition in all these measurements appears at around the same temperature, 5.72 ± 0.02 K. A vertical dotted line is drawn through all the plots to indicate the superconducting (SC) transition temperature ($T_{SC}$) in the different measurements. The SC anomaly in $C_{ac}(T)$ is found to be quite small compared to other properties. In the inset of the Fig. 2, an expanded view near the phase transition is displayed which shows a clear anomaly in $C_{ac}(T)$ at $T_{SC}$. A dash-dotted line has also been drawn above the transition in Fig. 2(c) to exhibit the change in slope between the SC and normal state.

The temperature widths ($\Delta T_{SC}$) of the SC transition estimated from $\rho(T)$, $\chi_{ac}(T)$ and $C_{ac}(T)$ were within 40 mK and the corresponding uncertainty in pressure was within ±0.1 GPa. It implies that the pressure homogeneity and hence the hydrostaticity inside the cell was quite good. It is worth to mention that the SC transition widths, obtained from the different measurements, were found to be insensitive to pressures variation (except ac-susceptibility, see the discussion later). One may notice, from Fig. 2(a), small temperature dependent and nonzero resistivity below the SC transition. But this is clearly an artifact of our experiment. The nonzero value is due to the formation of a bridge between the voltage and the current leads through a small drop of silver paste which was added on top of the thermocouple junction to repair a faulty contact. Because of this problem, the transition temperature is defined as the average of the temperatures which correspond to 10% and 90% of the $\rho(T)$-onset from the normal to SC transition ($T_{SC}=\frac{T_{10\%}+T_{90\%}}{2}$). The same convention is used for the ac-susceptibility in Fig. 2(b), whereas for the ac-heat capacity the transition is determined by the onset of the SC transition. The transition widths for $\rho(T)$ and $\chi_{ac}(T)$ are defined as $\Delta T_{SC}=T_{90\%}^{\rho}-T_{10\%}^{\rho}$, and for $C_{ac}$ it is the temperature difference between the onset and the peak of the transition. The SC transition width obtained from the $C_{ac}$ was found to be the smallest, whereas the largest is obtained for the ac-magnetization measurement (excluding thermopower, where the comparatively large width comes from the externally applied temperature gradient). The small value of $\Delta T_{SC}$ found from $C_{ac}$ is most likely due to the fact that only a small part of the sample close to the heater is probed in this measurement. But for the ac-magnetization, we have probed the bulk property of almost the entire sample. The relatively sharp transition in $\rho$ compared to $\chi_{ac}$ may be explained by considering the fact that resistivity is not a bulk property—the smaller transition width is due to the electron conduction through a filamentary path which connects the lowest resistivity. Concerning thermopower in Fig. 2(d), only the onset of the transition is marked as $T_{SC}$. The broad transition width of almost 0.3 K reflects the relatively large thermal gradient (0.3 K) applied to get a sufficient signal. The noise in the thermopower measurement is quite large, nevertheless the SC transition is obvious. Due to the lack of a proven calibration of the absolute thermopower of Au and AuFe under pressure, we obtained a value of $S$ of about 0.15 μV/K in

![Figure 2](image-url)
the SC state. For the sake of presentation, $S(T)$ has been normalized to zero in the SC state, Fig. 2(d). The jump of $S(T)$ at $T_{SC}$ is found to be about 0.18 $\mu$V/K which is in satisfactory agreement with zero pressure measurements.\textsuperscript{8} Just above $T_{SC}$, the thermopower of Pb is weakly dependent on temperature and pressure. Due to the involvement of various uncertainties in the measurement process, we will not discuss any further results on $S(T)$ in the following text. Resistivity of Pb is already well studied\textsuperscript{9} and hence there is no need to present it again. The measurement of $\chi_{ac}(T)$ is new in this Bridgman-type cell with a liquid medium and this was our original motivation for this work. In the remaining part of this communication, we will, therefore, confine our discussion on ac-magnetization and ac-heat capacity.

### A. ac-calorimetry

A review of the technique is given in the Ref. 10 by Gmelin. This technique provides a sensitive measurement of the sample heat capacity even in highly nonadiabatic circumstances and is extremely suitable to be used inside a pressure cell. Its principle is to expose the sample to a periodic heating, and to monitor the resulting temperature oscillations. As presented in Fig. 1, the sample is thermally excited by a heater (H). A low-noise transformer (Model 1900, Princeton Applied Research) is used for preamplifying the signal from the thermocouple. The signal was then detected by a lock-in amplifier (Model SR830 DSP, Stanford Research Systems). In the ideal case, when the couplings among the heater, sample and thermometer are perfect (and when the heat capacities of the heater and the heat link are low), the temperature oscillations of the sample, $T_{ac}$, depends only on the applied frequency $\omega = (2\pi f)$, the specific heat of the sample $C$, and the global heat link $\kappa$ through the equation:

$$T_{ac} = \frac{|P_r/(\kappa + i\omega C)|}{\omega^2} , \quad (i^2 = -1),$$

(1)

where $P_r$ is the mean heater power. When working above the cut off frequency ($\omega_{cut-off} = \kappa/C$), i.e., where the sample effectivelly decouples from its surroundings, $T_{ac}$ is inversely proportional to $\omega^2 C$. Experimentally, $T_{ac}$ can be determined from the relation:

$$T_{ac} = \frac{V_{ac}}{S_{AuFe}},$$

(2)

where $V_{ac}$ is the voltage across the Au/AuFe thermocouple (measured by the lock-in) and $S_{AuFe}$ is the corresponding thermopower. For the sake of simplicity (and also because of lack of proven calibration of $S_{AuFe}$ under pressure), $C_{ac}(T)$ in Figs. 2(c) and 3, are plotted as the inverse of $V_{ac}$.

The cut off at low pressure (0.7 GPa) is found to be around 150 Hz and surprisingly, it is very similar to what was observed at ambient pressure (not shown here). But at higher pressure it increases rapidly and appears at around 2.3 kHz. This is, most probably, related to the fact that the thermal conductivity of the pressure medium, Daphne oil, changes drastically with applied pressure. A similar effect was also reported in ac-calorimetric experiments where liquid helium was used as pressure transmitting medium.\textsuperscript{11}

In Fig. 3, the ac-heat capacities are plotted at three different pressures. The SC transition is found to correspond roughly to a few nanovolts [e.g., $V_{ac}(T_{SC}+\Delta T)=V_{ac}(T_{SC}$ $-\Delta T)=2.6$ nV at 4.1 GPa with an oscillating current amplitude of 5.6 mA] and almost independent of $p$ (Fig. 3). The small jump (4%) near $T_{SC}$ in $C_{ac}(T)$, is also in agreement with earlier heat capacity measurements at ambient pressure where the adiabatic method was used.\textsuperscript{12} A better agreement is possible if one takes into account of the background contribution. In inset of the Fig. 3, the frequency dependence of the signal $V_{ac}$ is shown at two different temperatures: below and above the SC transition. The cut off frequency appears almost at the same frequency—around 2.3 kHz. It suggests that the cut off frequency is determined by the heat link $\kappa$, which mainly depends on the type of anvils used and the surrounding pressure medium (Daphne oil).

### B. ac-susceptibility

Using simple electrodynamics, it can be shown that the voltage change $V_{emf}$ across the secondary coil, during the normal to SC transition, yields:

$$V_{emf} = 2\pi f \eta \chi_{ac} B r^2,$$

(3)

where $\chi_{ac}$, $\eta$, $r$, and $B$ are susceptibility ($\chi_{ac}$=-1 in the SC state), effective filling factor, radius of the secondary coil and magnetic induction $B(=9 \times 10^{-5}$ T), respectively. The number of turns is indicated by $N$ and $f$ represents the operating frequency. The total emf generated, $V_{emf} = \sqrt{(V_1)^2+(V_2)^2}$, where $V_1$ and $V_2$ are the real and imaginary parts, was measured as a function of temperature. The voltage was measured using a lock-in technique, with a low-noise preamplifier. The applied frequency and driving field are $f \approx 830$ Hz and $H_{ac} \sim 1$ Oe, respectively. As seen in Fig. 4, the signal below and above the SC transition, at different applied pressures, are found to be independent of temperature. The change in the voltage during the transition from the normal to SC state is found to be about 10 nV. The value of the $V_{emf}$ is in quite good agreement with the theoretical expression given in Eq. (3) and it is found to be the same for all
applied pressures. The voltage jump across the secondary coil corresponds to a change in about 2%. This small change is due to the presence of the background and it is important to note that no background subtraction has been done in our experiment.

Above 3 GPa the transition width of $\chi_{ac}$ broadens a bit compared to that at lower pressure. This is probably related to a slight distortion of the coils due to the solidification of the Daphne oil and a concomitant degradation of the pressure condition. The variation of $T_{SC}$ with $p$, $dT_{SC}/dp = -0.35 \pm 0.01$ K/GPa with $T_{SC}(p=0) = 7.17 \pm 0.05$ K, is found to be very close to that reported by Eiling et al.\(^9\)

**IV. CONCLUSIONS**

We have developed and successfully tested a single experimental setup to measure simultaneously four different physical properties of a system under identical pressure condition. Unlike Teflon pressure cell, this is a one time experiment and the coils or part of the setup are not reusable. The gasket becomes plastic at high pressure. The liquid medium, while depressurization, escapes with full force through a small deformed place in the gasket, and thereby destroys all the contacts and the coil. The maximum pressure that can be achieved with the present cell is 7 GPa, though we were limited to 5 GPa due to electrical contact problem. Efforts to modify the cell to extend the pressure range above 10 GPa are already underway.

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\(^1\) A.-S. Rüetschi and D. Jaccard, Rev. Sci. Instrum. 78, 123901 (2007);