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Low-frequency ac measurement of the Seebeck coefficient

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We have analyzed the sources of error in the measurement of the Seebeck coefficient and designed a low frequency ac method to reduce them. This method has high precision in a short time period compared to commonly used dc methods while it minimizes some major sources of error that other ac methods do not. Furthermore, the setup can be fit into a 3 mm diam × 7 mm Teflon pressure cell and has minimal side effects due to the heat conductance of the pressure medium. We have also proposed and tested several methods to calibrate the Seebeck coefficient of thermocouples under pressure. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1406930]

I. INTRODUCTION

The Seebeck coefficient, also called the thermal emf coefficient, thermoelectric power (TEP) or thermopower, is the voltage generated across two points on a material divided by the temperature difference between the two points. The Seebeck effect and the Peltier effect, which are two mutually reversed effects, were widely used for temperature measurement, power generation and electronic refrigeration.[1,2] Besides being an important transport property, the Seebeck coefficient is also essential for understanding the physics of materials both theoretically and experimentally.[3,4] Therefore it is also important to measure the Seebeck coefficient fast and precisely.

For Seebeck coefficient measurements, direct current (dc) measurements usually need a relatively long waiting time for the temperature to stabilize, which makes the measurement inefficient. There are alternate current (ac) setups for the Seebeck coefficient measurement that were described by Howson *et al.*[5] We found that special care needs to be taken for ac over that of the dc method. We show that the ac heating method is crucial for getting the correct Seebeck coefficient, especially when $dS(T)/dT$ (S denotes the Seebeck coefficient, T denotes temperature) is large. We also show that this method is useful to measure the Seebeck coefficient under high pressure and show the importance of calibration under high pressure, which was usually neglected in previous work.

II. SETUP

A. General setup

The setup is shown in Fig. 1. Using indium two thermocouples (TCs) were attached to a sample, which had a typical size of 4 mm×1.5 mm×1.0 mm. The thermocouples used in our experiments were of KP/TP, KN/TP or TN/TP, where KP, KN, TN and TP are ANSI letter-designated thermoelements. We use TC wire 1 and TC wire 2 to represent them in later discussions; TC wire 2 is always TP, i.e., high-purity copper, wire. Two small heaters (Ru_2O film coated on a 2 mm×1.5 mm or smaller ceramic) were glued to the ends of the sample with GE 7031 varnish. The resistance of the heater is about 1 kΩ at room temperature and is temperature insensitive down to 50 K. The heater currents (I_a and I_b) that we chose are two orthogonal sinusoidal waves generated by two Keithley 220 current sources. The frequency can be varied but the typical frequency we used was 0.05 Hz. The frequency of the thermoelectric voltage generated is 0.1 Hz. The typical time constant (τ) for the temperatures of the sample ends to balance is 1–3 s. The Keithley 220 dc current source has 100 memory locations that can simulate a good sinusoidal wave with some high frequency components, which generate another ac temperature difference around 10 Hz. Compared to the τ of 1–3 s, this relatively high frequency generates a very low thermal response. Three independent signals, V_{W1} (the voltage between TC wires 1), V_{W2} (the voltage between TC wires 2) and V_T (the voltage of one of the thermocouple pairs), were measured by Keithley 181/182/2182 or Hewlett Packard 34420A nanovoltmeters. The signals were recorded versus time. The voltages V_{W1} and V_{W2} were good sinusoids as expected. The temperature–voltage relation for the thermocouple pair, $\mathcal{T}_{\mathrm{TC}}(V)$, was calibrated with a very slow cooling/warming rate. From the $\mathcal{T}_{\mathrm{TC}}(V)$ curve, one can get the difference between $S_{W1}(T)$ (the thermopower of TC wire 1) and $S_{W2}(T)$ (the thermopower of TC wire 2). Then $S_{W1}(T)$ was calibrated by pure Pb, using the absolute thermopower data of Pb from Ref. 6. The thermopower of the sample (S) can be extracted by solving

$$V_{W1}=(S-S_{W1})\Delta T, \tag{1}$$

$$V_{W2}=(S-S_{W2})\Delta T, \tag{2}$$

$$T=\mathcal{T}_{\mathrm{TC}}\left(V_T+\frac{V_{W2}-V_{W1}}{2}\right). \tag{3}$$

B. Reducing the errors

Many things can cause, sometimes huge, errors. A Fourier transformation might help us to elucidate the special errors that only appear in an ac measurement.

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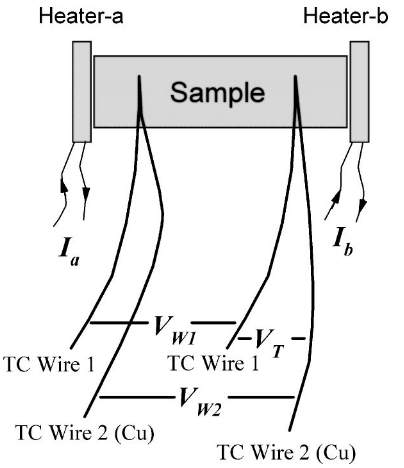

FIG. 1. Setup for TEP measurement. Each pair of thermocouple wires was sputter welded then attached to the sample to make electrical contact by direct welding, silver epoxy or indium.

Suppose the temperatures of the two ends of the sample are T_A and T_B, such that

$$T_A=\overline{T}+\frac{\Delta T}{2}+\tilde{T}_A\cos\omega t, \tag{4}$$

$$T_B=\overline{T}-\frac{\Delta T}{2}+\tilde{T}_B\cos\omega t, \tag{5}$$

where $\overline{T}$ is the time average of the base temperature of the sample, ΔT is the dc temperature difference, $\delta T=\tilde{T}_A-\tilde{T}_B$ represents the ac temperature gradient, while $\tilde{T}=(\tilde{T}_A+\tilde{T}_B)/2$ represents the ac component of the base temperature of the sample, i.e., the base temperature fluctuation.

We can derive (see the Appendix):

$$S_{\text{measured}}-S(\overline{T})\approx S'(\overline{T})\frac{\tilde{T}\cdot\Delta T}{\delta T}, \tag{6}$$

where S_{measured} is the measured experimental quantity for the relative thermopower, $S(\overline{T})$ is the thermopower for the temperature $\overline{T}$, while $S'(\overline{T})$ is the derivative of $S(T)$ at temperature $\overline{T}$.

From Eq. (6), we can easily see that when the dc temperature difference across the sample and the base temperature fluctuation across the sample are large compared to the ac temperature difference across the sample, and/or when $S'(T)$ is big, e.g., near the superconducting transition temperature, this term could be very large. Note that usually the smaller ac temperature difference δT is, the finer resolution versus temperature will be. This is the case we desire according to common sense. In such a case, though, the problem is more serious. One of the common wrong choices is to use a high frequency, in which case the ac temperature gradient across the sample is very small, while the result is seemingly satisfactory because the signal is relatively easy to measure at high frequency such as 1–10 Hz. In such a case, the dc temperature difference across the sample, ΔT, is usually much larger compared to the ac one, δT. In the conventional heat sink method (i.e., heat sinking of one sample end and heating at the other end) the base temperature fluctuates as half of the ac temperature gradient, i.e., $\tilde{T}\approx\delta T/2$.

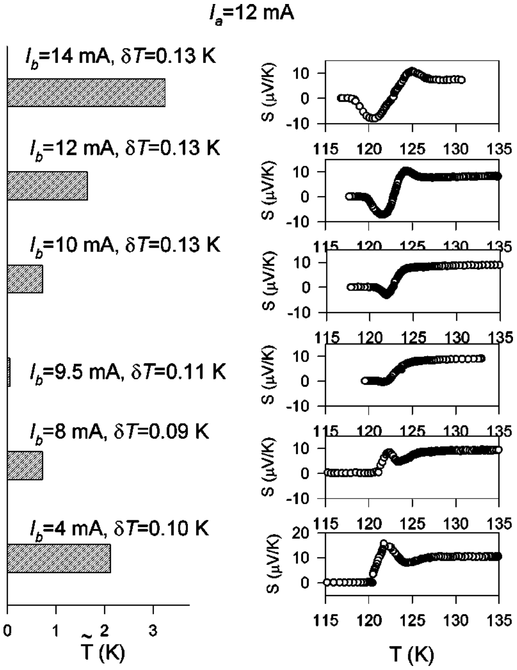

FIG. 2. Error for ac thermopower measurement due to fluctuation of the sample average temperature. The charts on the left show the base temperature fluctuation $\tilde{T}$. The graphs on the right show corresponding curves for the Seebeck coefficient measured with such an error. δT in the charts on the left represents the ac temperature gradient.

To show this problem convincingly, we did a test measurement on a $HgBa_2CaCu_2O_{6-\delta}$ sample. The sample is very irregularly shaped, and thus it is not easy to minimize the dc temperature difference ΔT by simply equalizing heater currents I_a and I_b. The ac temperature difference δT is ~ 0.11 K in our measurement. By adjusting heating currents I_a and I_b at the two ends of the sample, we can control the base temperature fluctuation $\tilde{T}$. The result is shown in Fig. 2. The I_a was 12 mA in all cases, while I_b was decreased from 14 to 4 mA. The left bar chart in Fig. 2 shows the change of $\tilde{T}$. We can see that it decreases from about 3 to $\lesssim$ 0.05 K, and then it goes back up to $\approx$ 2 K. The right side shows the S vs T curve for each case near the superconducting transition temperature. We can clearly see that, when $\tilde{T}$ is not small, the thermopower has a weird wrong shape, while when $\tilde{T}$ is less than 0.05 K, the curve of the ac measurement is similar to that of other high temperature superconductors. A dc measurement gives the same S vs T curve as the fourth curve in Fig. 2, which verifies our conclusion. Equation (6) was able to simulate the weird shapes in Fig. 2 successfully using the dc measured S vs T, experimentally measured $\tilde{T}$, δT and a reasonable value of ΔT.

We found in work reported Ref. 5 that a similarly shaped Seebeck coefficient anomaly showed through the transition. In those experiments, the frequency was 6 Hz, and the ac root mean square (rms) temperature gradient was about 50 mK. These authors also used the heat sink method, which will give $\tilde{T}\approx\delta T/2$ as we argued above. There was much discussion of the results of Ref. 5 in Refs. 7 and 8 and our result also disagrees with that in Ref. 5.

In our method, these problems are eliminated. For heating currents I_a and I_b at the two ends of the sample, we have

$$I_A = I_0 \cos \omega t, \tag{7}$$

$$I_B = I_0 \sin \omega t. \tag{8}$$

The power of the heating is $P = I^2 R/2$, where R is the resistance of the heater, so we have

$$P_A - P_B = I_0^2 R \cos 2\omega t, \tag{9}$$

$$P_A + P_B = I_0^2 R, \tag{10}$$

$$\overline{P_A} = \overline{P_B}. \tag{11}$$

Now suppose the sample is symmetric in both shape and heat coupling. Equation (9) induces the ac temperature difference δT. Equation (10) ensures that the total heating of the sample does not change over time, i.e., in the ideal case, the base temperature fluctuation of the sample $\tilde{T}$ is zero. Equation (11) ensures that the dc heating powers at the two ends of the sample are the same, which, ideally gives zero ΔT due to heating. In the real case, the sample shape or the heat coupling between the heater and the sample might not be symmetric, so we can adjust the heating current of the heaters to minimize the base temperature fluctuation, which was demonstrated in Fig. 2.

Note that, in the general setup,[9] it is required that the thermocouple wires be insulated from the sample electrically, while being thermally conducting. In our method, TC wire 1 actually touches TC wire 2 (copper) and the sample electrically, which ensures that the thermocouple that measures the temperature difference is very close to the points that generate thermal voltage across the sample. As a result, the vacuum environment that is usually required is no longer necessary; the sample and the thermocouples can even be surrounded by a heat conducting medium.

Our ac method is quite satisfactory. The typical measurement noise is less than 10 nV/K, and the repeatability on a given sample is within 0.1 μV/K even with the repositioning of leads and heaters. For measurements from 20 to 300 K, the time required to finish the measurement is only a few hours. Slower cooling/heating achieves more precise results. Our method also has some other advantages, e.g., it only requires two pairs of thermocouples to get three independent signals; it does not require a long wait at each temperature for stabilization, slow cooling/warming is the only requirement on temperature; it does not require a vacuum environment; it can be easily adapted for measurements up to temperatures of 500 K or more; it can also be adapted for measurements under high pressure; it can monitor the base temperature fluctuation during measurement, and predict the possible incorrect results common to the ac method; moreover, it can minimize/eliminate base-temperature fluctuation by adjusting the current of the two heaters.

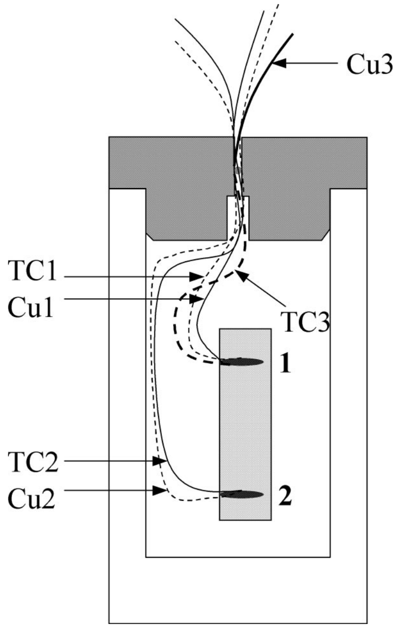

FIG. 3. Setup for TEP measurement under pressure. Point 3 is the hole in the Be–Cu cap that was sealed by epoxy. The cap can be treated as isothermal and point 3 is where the pressure changed from P to 0.

III. MEASUREMENT OF THE SEEBECK COEFFICIENT UNDER PRESSURE

The setup is similar to that described in Sec. II A except that the sample is in a Teflon pressure cell. Such a setup, though, does not give the correct temperature for the sample unless there is information on the portion of thermal voltage contributed from the part of thermocouples inside the pressure cell. In order to obtain such information, an additional thermocouple should be added to measure the temperature difference because of applied pressure on the thermocouple inside the pressure cell (Fig. 3). Two pairs of thermocouples (Cu1/TC1 and Cu2/TC2) were attached to the sample at points 1 and 2. (Here we use TC to denote thermocouple wire 1 and Cu to denote thermocouple wire 2 the same as in earlier discussion.) An additional thermocouple wire, TC3, was attached at point 1 and sputter welded to another Cu wire (Cu3) at point 3, where the pressure changes to ambient pressure. Another nanovoltmeter was used to measure the signal between Cu1 and Cu3 to get the temperature difference between points 1 and 3. When the pressure effect of thermopower on the thermopower of the thermocouple pair is small, the temperature difference between point 1 and point 3 can be neglected, i.e., one can use the thermopower data of thermocouples at ambient pressure to determine the base temperature of the sample. In this case, one should bear in the mind that there will be an error using this approximation and always estimate it if it will be crucial to the measurement.

More sources of error need to be considered for thermopower measurements under pressure. For example, due to the heat conducting environment, it is very important to make sure that the temperature difference measured is very close to that which generates the thermal voltage. The method mentioned in Sec. II A was chosen to minimize such an error. Since the TC wire 1 actually touches TC wire 2 (copper) and the sample electrically, one can arrange them much closer than in the general case,[9] which requires insulation between thermocouple wires 1 and 2.

Another intrinsic source of error, which was neglected in most previous work, is that of the change of thermopower of thermocouples under pressure. From Eqs. (1)–(3), we get

$$S=\frac{V_{W2}}{V_{W1}-V_{W2}}\cdot(S_{W1}-S_{W2})+S_{W2}. \tag{12}$$

The thermopower we measured this way is a relative value to the thermopower of thermocouple wire 1 and copper, which also changes under pressure.

IV. CALIBRATION OF THE SEEBECK COEFFICIENT UNDER PRESSURE

A. Self-calibration using a pair of miniature thermometers

In order to calibrate the thermopower of these thermocouples, we have used a "self-calibration" method. We calibrated two homemade platinum wire resistors very carefully under pressure. Since we changed the temperature at a very slow rate, the thermocouples inside the pressure cell are isothermal. Thus the temperature measured using the thermopower data at ambient pressure is accurate. This calibration turned out to be very repeatable. After we calibrated the resistors using the thermocouples, we used the resistors to measure the temperature difference and calculate $S_{W1}(P)-S_{W2}(P)$. Notice that such a calibration, although requiring extreme care, is not as difficult as one might think. The temperature difference we measured is $\mathcal{T}^a(V^a)-\mathcal{T}^b(V^b)$; the very small error in the calibration of $\mathcal{T}^a(V)$ and $\mathcal{T}^b(V)$ is increased by subtraction. The method we use relies on the value $[\mathcal{T}^a(V_1^a)-\mathcal{T}^b(V_1^b)]-[\mathcal{T}^a(V_2^a)-\mathcal{T}^b(V_2^b)]$, which can be rewritten as $[\mathcal{T}^a(V_1^a)-\mathcal{T}^a(V_2^a)]-[\mathcal{T}^b(V_1^b)-\mathcal{T}^b(V_2^b)]$. We can see that the requirement of the calibration is less rigorous since the possible systematic error on $\mathcal{T}^a(V^a)$ or $\mathcal{T}^b(V^b)$ cancels out. The change of $S_{W2}(P)$ with pressure is small and negligible.[10] Our actual calibration turned out to have about 0.7%/GPa uncertainty and is the major error of the TEP measurement under pressure.[11] It is due to the fact that it is hard to make the temperature at Pt sensors the same as the temperature at the end of thermocouples inside the pressure cell, i.e., in this calibration, the drawback of a conventional setup[9] is not avoided.

B. Heat-cycle method

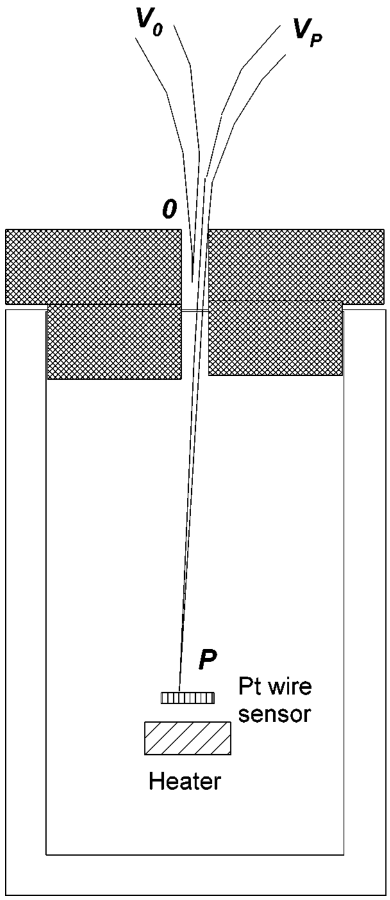

FIG. 4. Heat-circle method for calibration of thermocouples under pressure. A miniature platinum wire temperature sensor was located close to the end of the thermocouple.

Another method for calibration is shown in Fig. 4. Two pairs of thermocouples were used. Thermocouple pair 0 is on the cap of the Teflon pressure cell, and thermocouple pair P is inside the pressure cell with a miniature Pt wire temperature sensor attached to it. The voltages relative to a certain reference temperature T_{ref} is a state function $V=\mathcal{F}(T)$ of the temperature T, and the inverse function $\mathcal{F}^{-1}(V)$ exists. Let $S(T)$ be the relative thermopower $S_{W1}(T)-S_{W2}(T)$, $S_0(T)$ be the relative thermopower at ambient pressure, $S_P(T)$ be the relative thermopower under pressure, and $\Delta S(T)=S_P(T)-S_0(T)$ be the difference in thermopower under pressure that we want to calibrate, then we have

$$S_0(T)=\frac{\mathrm{d}\mathcal{F}(T)}{\mathrm{d}T}, \tag{13}$$

$$\frac{1}{S_0(T)}=\frac{\mathrm{d}\mathcal{F}^{-1}(V)}{\mathrm{d}V}\Big|_{V=\mathcal{F}(T)}. \tag{14}$$

We measure the signal V_P between thermocouple P and the signal V_0 between thermocouple 0, which can be considered to be at ambient pressure, together with the resistance R of the Pt wire resistor sensor.

Since,

$$V_P=\int_{T_{\text{ref}}}^{T_0}S_0(T)\,\mathrm{d}T+\int_{T_0}^{T_P}S_P(T)\,\mathrm{d}T, \tag{15}$$

we have

$$\begin{aligned}\mathcal{F}^{-1}(V_P)&=\mathcal{F}^{-1}\left(\int_{T_{\mathrm{ref}}}^{T_0} S_0(T)\,\mathrm{d}T+\int_{T_0}^{T_P} S_P(T)\,\mathrm{d}T\right)\\&\approx\mathcal{F}^{-1}\left(\int_{T_{\mathrm{ref}}}^{T_P} S_0(T)\,\mathrm{d}T+\Delta S(T_P)(T_P-T_0)\right)\\&=\mathcal{F}^{-1}(\mathcal{F}(T_P)+\Delta S(T_P)(T_P-T_0))\\&=T_P+\frac{\mathrm{d}\mathcal{F}^{-1}(V)}{\mathrm{d}V}\Big|_{V=\mathcal{F}(T_P)}\cdot\Delta S(T_P)(T_P-T_0)\\&=T_P+\frac{\Delta S(T_P)}{S(T_P)}\cdot(T_P-T_0).\end{aligned}\tag{16}$$

If we have two, taken as A and B, sets of different data of V_0 and V_P at the same temperature T_P, which can be determined by maintaining the same R as that for the Pt wire, we have

$$\mathcal{F}^{-1}(V_P^A)=T_P+\frac{\Delta S(T_P)}{S(T_P)}\cdot(T_P-T_0^A),\tag{17}$$

$$\mathcal{F}^{-1}(V_P^B)=T_P+\frac{\Delta S(T_P)}{S(T_P)}\cdot(T_P-T_0^B).\tag{18}$$

Subtracting the above two equations, we get

$$\begin{aligned}\frac{\Delta S(T_P)}{S(T_P)}&=-\frac{\mathcal{F}^{-1}(V_P^A)-\mathcal{F}^{-1}(V_P^B)}{T_0^A-T_0^B}\\&=-\frac{\mathcal{F}^{-1}(V_P^A)-\mathcal{F}^{-1}(V_P^B)}{\mathcal{F}^{-1}(V_0^A)-\mathcal{F}^{-1}(V_0^B)}\\&\approx-\frac{V_P^A-V_P^B}{V_0^A-V_0^B}.\end{aligned}\tag{19}$$

So the procedure of calibration using this method is very simple, but it requires great care, since we need to measure $V_P^A-V_P^B$ very precisely. By turning on the heater and ramping up the temperature slowly, we get two curves, V_0 vs R and V_P vs R. Then by turning off the heater and ramping up the temperature, we get another set of curves. For each R, we can thus have four voltages that can be used to get ΔS from Eq. (19). This method, though, has a limitation in that it can only calibrate $S_{W1}-S_{W2}$. Considering that S_{W2}, or S_{Cu}, changes little under pressure,[10] this is still a good method of calibration.

C. Cell-in-cell method

To achieve higher accuracy in the thermopower calibration under pressure, a differential method is desired. Bridgeman used such a method to measure the thermopower of some metals under pressure.[10] In Bridgeman's setup, two parallel long cylinders were used, and two identical thermocouples were fed through these two cylinders. Pressure was applied to one of the cylinders and a temperature gradient was generated between the ends of the cylinders. The voltage measured between these two identical thermocouples was directly caused by the change in thermopower under high pressure. Bridgeman's setup was not suitable for low temperature measurements. In order to use the differential method in our pressure cell, we propose a cell-in-cell method (Fig. 5). Inside the usual Teflon pressure cell, we have another Be–Cu cell, which has two small openings at both sides. The thermocouple wire to be calibrated, e.g., TC wire 1, is fed through the Be–Cu cell which is ambient or zero pressure, sputter welded to TC wire 2, and sealed with epoxy at both ends. Since the inner cell will not be pressurized when the Teflon cell is pressurized, the voltage between TC wire 1, V_{W1}, is generated differentially by the applied pressure, while V_{W2} is used to measure the temperature difference. The thermopower data at ambient pressure can be used to determine the temperature difference from V_{W2} by a first-order approximation. A few simple recursions would achieve higher precision if necessary.

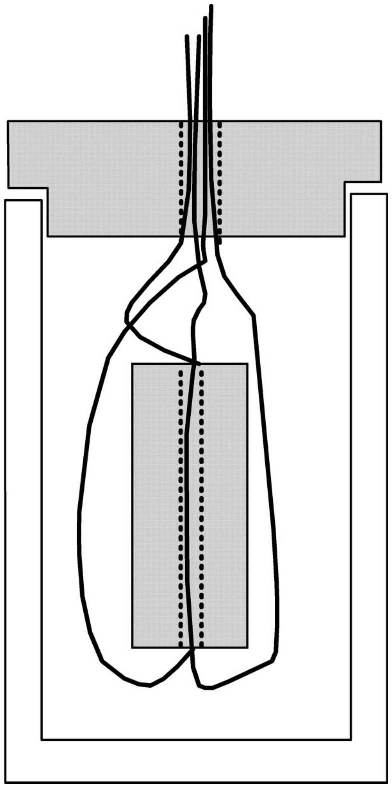

FIG. 5. Cell-in-cell method for calibration of thermocouples under pressure. A Be–Cu cylinder was put inside the Teflon pressure cell. The medium inside the Teflon pressure cell was pressurized, while the smaller Be–Cu cell was sealed by epoxy and kept at ambient or lower pressure while the whole setup was cooled.

Compared to the self-calibration method, the cell-in-cell method requires both thermal and electrical contact, thus minimizing the effect of the heat conducting pressure medium, which was the major source of error in the self-calibration method. Compared to the heat-circle method, the cell-in-cell method is a true differential method, and thus does not require subtraction of two large voltages to get the small signal. In addition, one can switch TC wires 1 and 2 in our setup and calibrate TC wire 2. For the heat-circle method, the setup and measurement are simplest, but only the difference between TC wires 1 and 2 can be calibrated.

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APPENDIX: FIRST-ORDER FOURIER ANALYSIS FOR ac THERMOPOWER MEASUREMENT

Suppose the temperatures of the two ends of sample are T_A and T_B, such that

$$T_A=\overline{T}+\frac{\Delta T}{2}+\tilde{T}_A\cos\omega t, \tag{A1}$$

$$T_B=\overline{T}-\frac{\Delta T}{2}+\tilde{T}_B\cos\omega t. \tag{A2}$$

where $\overline{T}$ is the time average of the base temperature of the sample, ΔT is the dc temperature difference, $\delta T=\tilde{T}_A-\tilde{T}_B$ represents the ac temperature gradient while $\tilde{T}=(\tilde{T}_A+\tilde{T}_B)/2$ represents the ac component of the base temperature of sample, i.e., the base temperature fluctuation.

The voltages relative to a certain reference point at places A and B, V_A and V_B, are a state function $\mathcal{F}(T)$ of temperatures T_A and T_B. We have

$$S(T)=\frac{d\mathcal{F}(T)}{dT}, \tag{A3}$$

$$S_{\text{measured}}=\frac{\tilde{V}_A-\tilde{V}_B}{\tilde{T}_A-\tilde{T}_B} \tag{A4}$$

$$=\frac{\frac{1}{\pi}\int_0^{2\pi}(V_A-V_B)\cos\omega t\cdot d(\omega t)}{\delta T}, \tag{A5}$$

where $S(T)$ is the relative sample thermopower and S_{measured} is the measured relative thermopower.

We have,

$$V_A-V_B=\mathcal{F}(T_A)-\mathcal{F}(T_B) \tag{A6}$$

$$\approx\frac{d\mathcal{F}(T)}{dT}\bigg|_{\overline{T}}\cdot(T_A-\overline{T})+\frac{1}{2}\frac{d^2\mathcal{F}(T)}{dT^2}\bigg|_{\overline{T}}\cdot(T_A-\overline{T})^2$$
$$-\frac{d\mathcal{F}(T)}{dT}\bigg|_{\overline{T}}\cdot(T_B-\overline{T})-\frac{1}{2}\frac{d^2\mathcal{F}(T)}{dT^2}\bigg|_{\overline{T}}\cdot(T_B-\overline{T})^2$$
$$=S(\overline{T})\cdot\left(\frac{\Delta T}{2}+\tilde{T}_A\cos\omega t\right)+\frac{1}{2}S'(\overline{T})\cdot\left(\frac{\Delta T}{2}+\tilde{T}_A\cos\omega t\right)^2$$
$$-S(\overline{T})\cdot\left(-\frac{\Delta T}{2}+\tilde{T}_B\cos\omega t\right)-\frac{1}{2}S'(\overline{T})\cdot\left(-\frac{\Delta T}{2}+\tilde{T}_B\cos\omega t\right)^2$$
$$=S(\overline{T})\cdot\delta T\cdot\cos\omega t+S(\overline{T})\cdot\Delta T+\frac{1}{2}S'(\overline{T})\cdot(\tilde{T}_A-\tilde{T}_B)\cdot(\tilde{T}_A+\tilde{T}_B)\cdot\cos^2\omega t+\frac{1}{2}S'(\overline{T})\cdot(\tilde{T}_A+\tilde{T}_B)\cdot\Delta T\cdot\cos\omega t$$
$$=S(\overline{T})\cdot\delta T\cdot\cos\omega t+S(\overline{T})\cdot\Delta T+S'(\overline{T})\cdot\delta T\cdot\tilde{T}\cdot\cos^2\omega t+S'(\overline{T})\cdot\tilde{T}\cdot\Delta T\cdot\cos\omega t. \tag{A7}$$

Thus,

$$\frac{1}{\pi}\int_0^{2\pi}(V_A-V_B)\cos\omega t\cdot d\omega t$$
$$=\frac{1}{\pi}\left[\int_0^{2\pi}S(\overline{T})\cdot\delta T\cos^2\omega t\cdot d\omega t+\int_0^{2\pi}S(\overline{T})\cdot\Delta T\cos\omega t\cdot d\omega t+\int_0^{2\pi}S'(\tilde{T})\cdot\delta T\cdot\overline{T}\cos^3\omega t\cdot d\omega t+\int_0^{2\pi}S'(\tilde{T})\cdot\tilde{T}\cdot\Delta T\cos^2\omega t\cdot d\omega t\right]$$
$$=S(\overline{T})\cdot\delta T+S'(\overline{T})\cdot\tilde{T}\cdot\Delta T. \tag{A8}$$

Recalling Eq. A5, we have

$$S_{\text{measured}}-S(\overline{T})\approx S'(\overline{T})\frac{\tilde{T}\cdot\Delta T}{\delta T}, \tag{A9}$$

where S_{measured} is the measured experimental quantity for the relative thermopower, while $S(\overline{T})$ is the thermopower for temperature $\overline{T}$.

[1] D. K. C. MacDonald, *Thermoelectricity: An introduction to the Principles* (Wiley, New York, 1962).
[2] H. J. Goldsmid, *Electric Refrigeration* (Temple, London, 1986).
[3] J. M. Ziman, *Principles of the Theory of Solids* (Cambridge University Press, New York, 1972).
[4] Q. Xiong *et al.*, Physica C **231**, 233 (1994).
[5] M. A. Howson *et al.*, Phys. Rev. B **41**, 300 (1990).
[6] R. B. Roberts, Philos. Mag. **36**, 91 (1977).
[7] G.Y. Logvenov, V. V. Ryazanov, R. Gross, and F. Kober, Phys. Rev. B **47**, 15322 (1993).
[8] M. A. Howson, Phys. Rev. B **47**, 15324 (1993).
[9] V. V. Rao, G. Rangarajan, and R. Srinivasan, J. Phys. F: Met. Phys. **14**, 973 (1984).
[10] P. W. Bridgeman, *The Thermodynamics of Electrical Phenomena in Metals, and a Condensed Collection of Thermodynamic Formulas* (Dover, New York, 1961).
[11] F. Chen, Q. M. Lin, Y. Y. Xue, and C. W. Chu, Physica C **282**, 1245 (1997).