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Low-temperature thermoelectrical power measurements using analogue subtraction

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Abstract. A simple, inexpensive analogue subtraction method for measuring thermoelectrical power from 4 to 300 K using two chromel (KP)/Au–7 at% Fe (Au:Fe) thermocouples is described. The average sample temperature is varied by lowering a small insert probe into a liquid-He-storage container or raising the probe. Details concerning the interface of the experiment to a personal computer are presented. Data collected on constantan, $Bi_2Sr_2CaCu_2O_{7+\delta}$ and carbon-nanotube samples show the utility of the method.

Keywords: thermoelectrical power, temperature, cryogenic, analogue subtraction, standards and calibration

1. Introduction

Pulse [1–3] and ac [4, 5] techniques are commonly used in thermoelectrical power measurements for inducing a time-dependent temperature gradient in order to reduce or eliminate errors due to drifting zero shift in dc amplifiers. In a much earlier publication [6] (see the discussion in [7]), we reported a heat-pulse method employing a simple analogue-subtraction circuit using three instrumentation amplifiers to measure the Seebeck coefficient as a function of temperature. This simple, inexpensive method requires only two thermocouples, which make electrical contact to the sample and this direct electronic coupling to the sample improves the thermal contact as well. In its original form published several years ago [6], this approach was used in the range $77 < T < 700$ K accessible to ordinary thermocouple systems such as chromel–alumel (K-type) and copper–constantan (T-type) thermocouples and required an X–Y plotter to record the thermoelectrical response of the sample. Here we report the interface of the thermoelectrical experiment to a PC and the extension of the experiment to 4 K using chromel (KP)/Au:Fe thermocouples. Seebeck-coefficient (or thermopower) data between 4 and 300 K were obtained by simply lowering the probe slowly into a liquid-He-storage container. The thermopower for a variety of samples (metals, standard oxide superconductors and carbon nanotubes) has been measured, which shows the utility of this approach.

2. Experimental details

2.1. The thermoelectrical circuit

Figure 1 shows the three thermoelectrical voltages ΔV_1, ΔV_2 and ΔV_3 which determine the absolute thermoelectrical power of the sample, S_U and the average sample temperature T. Using the definition of the thermoelectrical power S, the voltage difference ΔV developed between positions z_1 and z_2 in a homogeneous material with temperature profile $T(z)$ is given by

$$\Delta V = V(z_2) - V(z_1) = \int_{z_1}^{z_2} S \frac{\mathrm{d}T}{\mathrm{d}z}\,\mathrm{d}z \qquad (1)$$

where $V(z_1)$ and $V(z_2)$ are the voltages at z_1 and z_2 respectively. The voltages in figure 1 can therefore be written as

$$\Delta V_1 = \int_{T_0}^{T} S_A\,\mathrm{d}T + \int_{T}^{T+\Delta T} S_U\,\mathrm{d}T + \int_{T+\Delta T}^{T_0} S_A\,\mathrm{d}T = \int_{T}^{T+\Delta T} (S_U - S_A)\,\mathrm{d}T = (S_U - S_A)\Delta T \qquad (2)$$

$$\Delta V_2 = \int_{T_0}^{T} S_A\,\mathrm{d}T + \int_{T}^{T_0} S_B\,\mathrm{d}T = \int_{T}^{T_0} (S_B - S_A)\,\mathrm{d}T = V_{BA}(T) \qquad (3)$$

$$\Delta V_3 = \int_{T_0}^{T} S_B\,\mathrm{d}T + \int_{T}^{T+\Delta T} S_U\,\mathrm{d}T + \int_{T+\Delta T}^{T_0} S_B\,\mathrm{d}T = \int_{T}^{T+\Delta T} (S_U - S_B)\,\mathrm{d}T = (S_U - S_B)\Delta T. \qquad (4)$$

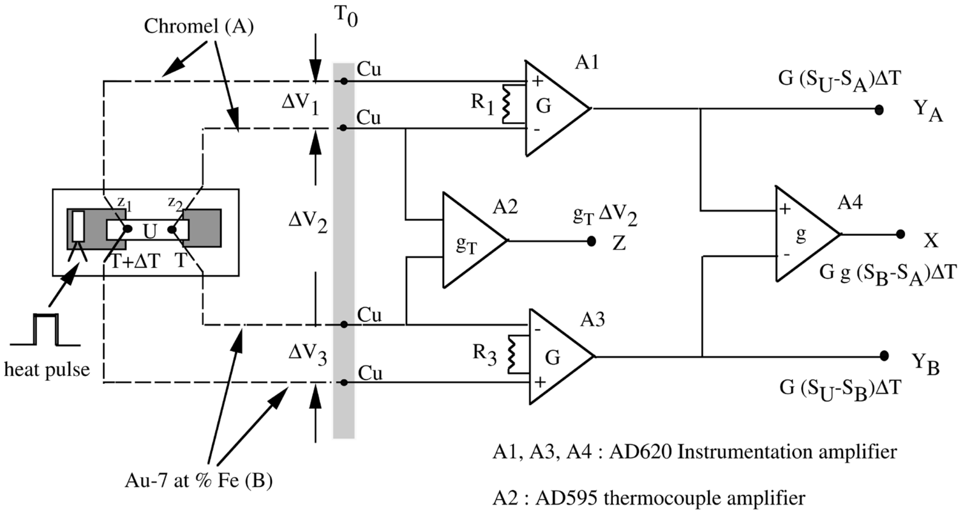

Figure 1. (*a*) A schematic diagram of the circuit. A heat pulse is applied to the sample (U) to establish a time-dependent temperature difference ΔT between the junctions of Au–7 at% Fe (B):chromel (A) thermocouples which make electrical contact with the sample. The thermocouple leads (broken lines) are thermally (but not electrically) anchored to the temperature reservoir at T_0. Cu leads then pass the thermoelectrical voltages (ΔV_1, ΔV_2 and ΔV_3) to amplifiers A_1, A_2 and A_3. The resistors R_1 and R_3 are used to match the gains of amplifiers A1 and A3. The amplifier gains (G, g_T and g) are labelled together with the inverting (−) and noninverting (+) inputs at the respective amplifiers. The amplifier outputs (Y_A, Y_B, X and Z) are fed to the PC for data processing.

The subscripts in equations (2)–(4) refer to either the thermocouple wire materials (A and B) or the sample (U). T_0 refers to the temperature of thermocouple junctions of A and B with copper leads that transfer the signals from this reservoir to the instrumentation amplifiers. The temperature T_0 is approximately the room temperature and is monitored with a type-K thermocouple with an electronic ice point. This additional thermocouple allows the slow drift in room temperature, which might affect T_0, to be taken into account.

2.2. The analogue subtraction circuit

In the new and improved circuit, we have used three Analog Devices, Inc, AD 620 instrumentation amplifiers (A1, A3 and A4) as shown in figure 1, for the analogue subtraction circuit [6]. Amplifiers A1 and A3 are constructed to have gains (G) of 1000. The variable resistors R_1 and R_3 allow their gains to be precisely matched. Amplifier A4 is constructed to have a gain (g) of 10. In order to determine the average sample temperature, the voltage ΔV_2 is measured as the output of the amplifier A2 (with gain g_T).

2.3. The heat-pulse generator

A heat-pulse generator with variable pulse width and height was built using a PIC 16C56 micro controller (Microchip Technology, Inc), which can be triggered by an external TTL signal. The pulse height and duration are adjustable in the ranges of 0–10 V and 1–20 s, respectively. Depending on the thermal mass of the sample and heater block, a temperature gradient of about 0.5 K is typically developed and relaxed over an interval of 5–20 s. A detailed circuit diagram of the heat pulse generator is available upon request.

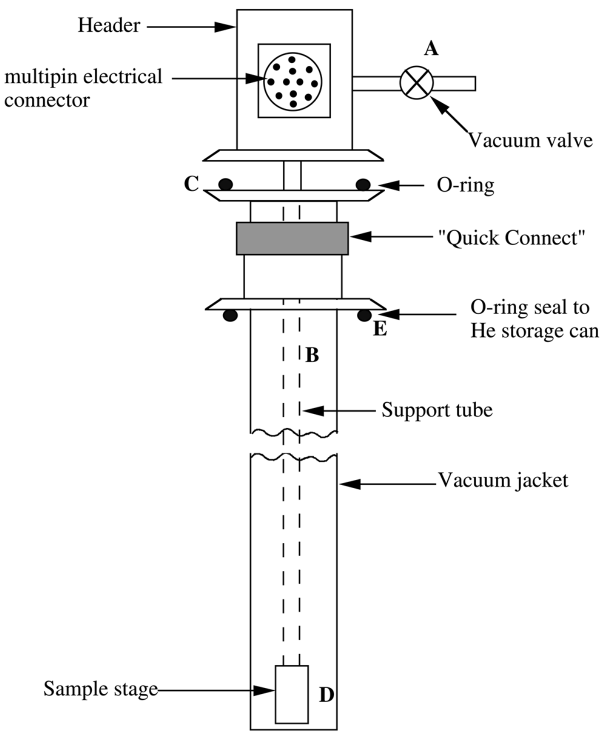

Figure 2. A schematic diagram of the thermopower-measurement probe suitable for the temperature range 4–300 K. See the description in the text.

2.4. The thermopower probe

The thermopower probe is shown schematically in figure 2. The overall probe length is 160 cm, which allows the insertion of it into an ordinary liquid-helium-storage container. The probe consists of a header with a hermetic multipin connector for electrical input/output and a vacuum valve at A.

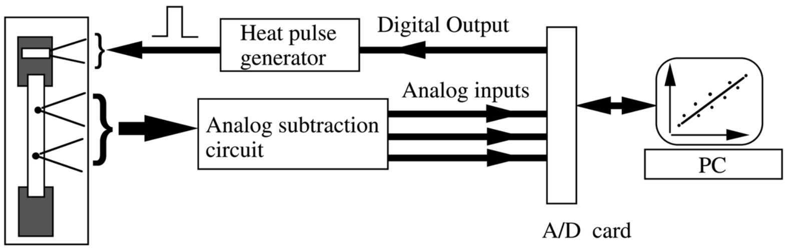

Figure 3. A schematic diagram of the system for thermopower measurement by analogue subtraction. See the description in the text.

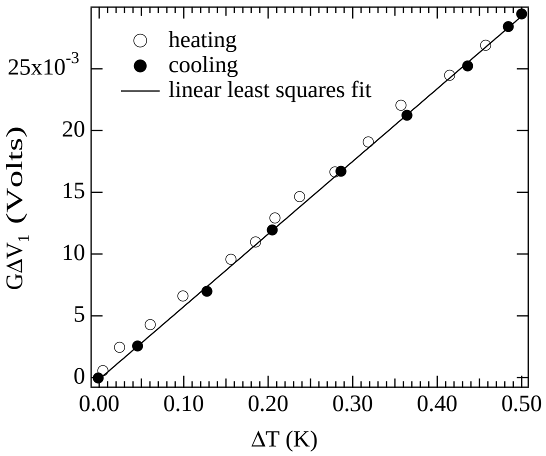

Figure 4. A plot of the thermoelectrical response versus the temperature gradient ΔT. Open and closed circles represent, respectively, data collected on heating and cooling. The full line is a linear least-squares fit to the data and the slope of this line is the relative sample thermopower.

The sample is mounted on a piece of Cu-clad fibre-glass circuit board which is, in turn, fastened to a stainless-steel stage on the end (D) of a 0.635 cm outer diameter, thin-walled stainless-steel tube (B) attached to the header. An O ring (C) seals the vacuum jacket (160 cm $\times$ 2.5 cm outer diameter thin-walled stainless-steel tube) to the header. Cu leads (0.0127 cm diameter) connect the sample heater at D to the multipin electrical connector on the header. Similarly, 0.0076 cm diameter thermocouple leads (Omega, Inc) carry the sample thermoresponse to the multipin connector and from there via copper leads to the analogue-subtraction amplifiers. A type-K thermocouple is anchored thermally to two unused pins on the hermetic connector and is used to measure the temperature T_0 (see figure 1) of the copper–sample thermocouple lead junctions (i.e. A–Cu and B–Cu). T_0 together with the relative thermopower of the chromel/Au:Fe couple is used to compute the average sample temperature T. Typically, the sample is installed on the stage, as described above and the probe is evacuated and back-filled with about 50 mTorr of He gas and then inserted into the He-storage can through a ‘quick connect’ O-ring seal (E). The sample temperature is decreased (increased) by slowly lowering (raising) the probe in the storage can. It typically takes 2 h to collect a total of 40–60 data points on cooling and also on warming cycles between 4 and 300 K. For each data point, the temperature is measured before and after the heat pulse is applied and the average temperature is evaluated. We make sure that the difference between the two readings is no more than 1 K. The proof that the heating and cooling rate is not too high is the linearity of Y_A (or Y_B) versus X which is a strict requirement on accepting a data point. Furthermore, we require that $S(T)$ data extracted from heating and cooling circles should overlap. In the event that they do not overlap, we suspect that there is a phase transition, a poor thermal contact or an excessively large cooling or heating rate.

3. Calibration and Seebeck-coefficient measurement

In a typical experiment, one end of the sample is placed in contact with a heat sink and the other end is in thermal contact with a heater. The two thermocouple junctions required are usually attached to the sample with silver paint or silver-containing epoxy resin. Figure 1 also shows a schematic representation of the sample holder. A 0.158 cm thick copper-clad fibre-glass circuit board is processed to leave two roughly 5 mm $\times$ 5 mm areas of copper, shown in figure 1 as shaded areas. A platinum resistor of type H2104 (Omega Engineering Inc) is thermally clamped, or silver-epoxied, onto one of the copper pads and serves as the heat source.

When the sample is at the desired stable temperature, the PC sends a TTL pulse via one of the digital output lines of the analogue-to-digital converter (A/D) card DAS8 (Keithley MetraByte) to trigger the pulse generator. As a result, a voltage pulse with appropriate width and height is applied to the heater, which causes a temperature gradient to develop and relax with time along the sample. Thermopower data are collected via the A/D card and PC as ΔT increases and relaxes. Typically, $\Delta T \sim 0.5$ K develops and dissipates in a time of 30 s. Figure 3 shows schematically the interface of the experiment to a PC via an A/D card. As shown in figure 1, the outputs X, Y_A (or Y_B) and Z were fed to the PC via the analogue inputs of the A/D card. For small temperature differences ($\Delta T < 0.5$ K), the plot of Y_A (or Y_B) versus X is a straight line whose slope is proportional to the sample thermopower measured with respect to the reference metal A (B), i.e., a relative thermopower $S_U - S_A$ or $S_U - S_B$. The data retrace themselves as the temperature gradient relaxes to zero. Data-acquisition software (ViewDac, Keithly MetraByte Inc) was used to calculate the slope of the thermoelectrical response using a linear least-square fitting algorithm, thereby determining the relative sample thermoelectrical power. Polling the output Z just before the heat pulse is started and after the heat pulse is terminated allows the average sample temperature to be calculated according to equation (3).

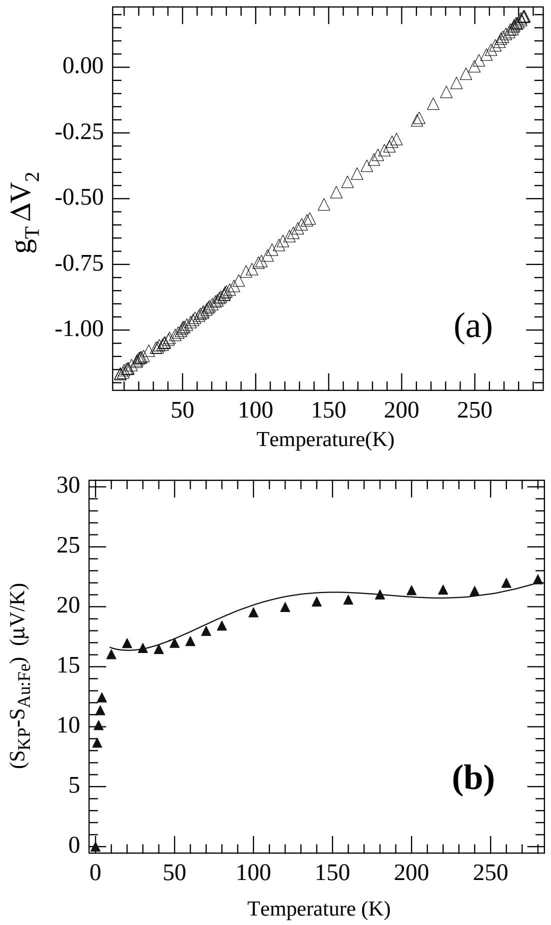

Figure 5. (*a*) V_{BA} as a function of the sample temperature T. (*b*) $\mathrm{d}(V_{BA})/\,\mathrm{d}T$ or $S_{KP} - S_{Au:Fe}$ versus T.

The output X is proportional to the sample temperature gradient ΔT.

The relative sample thermopower is related to the slope of the thermoelectrical response obtained by plotting Y_A and Y_B versus X:

$$slope_A = \frac{(S_U - S_A)G}{(S_B - S_A)Gg} \tag{5}$$

$$slope_B = \frac{(S_U - S_B)G}{(S_B - S_A)Gg}. \tag{6}$$

The quantities $S_B - S_A$, G and g are known from calibration experiments, which are checked every few weeks. Figure 4 depicts typical data collected for a test sample at $T = 300$ K. The open and closed circles are collected for increasing and decreasing ΔT. The straight line is the least-squares fit to the data. The calibration procedures for S_A, S_B and T are described briefly below.

One can make use of equation (3) to evaluate the sample temperature T via the quantity $S_{KP} - S_{Au:Fe}$. According to equation (3), the temperature-dependent relative thermopower of the thermocouple pair is given by

$$\frac{\mathrm{d}V_{BA}}{\mathrm{d}T} = S_{KP} - S_{Au:Fe}. \tag{7}$$

Therefore, by simply measuring the temperature dependence of the thermocouple voltage $V_{BA}(T)$ (equation (3)) and

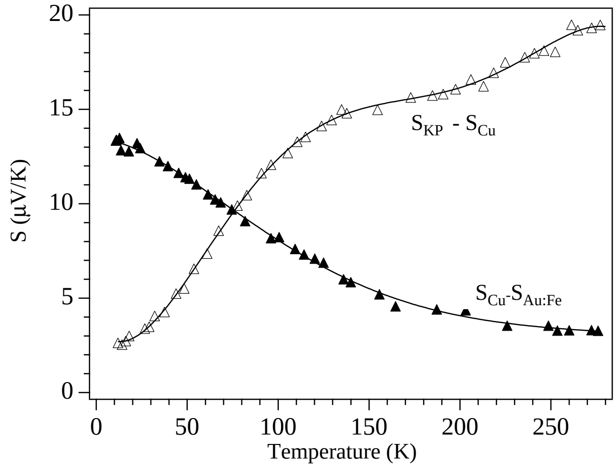

Figure 6. Experimentally determined $S_{KP} - S_{Cu}$ and $S_{Au:Fe} - S_{Cu}$ as functions of temperature T. Full lines represent the polynomial fits.

evaluating the derivative (equation (7)) in the computer, we can determine the temperature dependence of the KP–Au:Fe relative thermopower. This was done by attaching a KP–Au:Fe thermocouple with silver-containing epoxy resin to the surface of a silicon-diode thermometer (DT-470-SD-13-2S, LakeShore Cryotronics, Inc) and measuring the output voltage of amplifier A2 as a function of the temperature determined by the silicon-diode thermometer. The reference junction temperature (T_0) is needed for the calculation of the sample temperature T. Rather than using a cumbersome ice bath ($T_0 = 0\,^{\circ}$C), we opted to measure T_0 by thermally anchoring a type-K thermocouple to two pins on the hermetic connector. Usage of an ice bath at the reference junction allows one to determine the temperature directly from the ΔV_2 versus T calibration obtained using the Si diode. If T needs to be known to higher accuracy, perhaps a secondary thermometer such as a silicon diode should be used.

Although slow temperature drifts in room temperature T_0 can cause some error in absolute temperature, they are too slow to affect measurements of thermopower, because each data point is collected during a short period of time ($\simeq$20 s). Figure 5(*a*) displays the temperature dependence of the output voltage $V_{BA}(T)$ of the thermocouple amplifier (A2). These data are then fitted to a polynomial. Shown in figure 5(*b*) are the temperature derivative of the polynomial corrected for the gain (g_T) of amplifier A2 and, for comparison, previously published data [8] for $S_{KP} - S_{Au:Fe}$.

$S_U - S_A$ and $S_U - S_B$ are the sample thermopowers measured with respect to A (chromel) and B (Au:Fe), respectively. If data are desired only above 77 K are desired, then Cu:constantan thermocouples may be used [6] and the sample thermopower can then be measured directly with respect to copper. In the present case, the absolute thermopower S_U is finally obtained by using calibration data for $S_A(T)$ or $S_B(T)$. The absolute thermopower is obtained from the computer via equations (5) or (6). Having determined the quantity $S_{KP} - S_{Au:Fe}$, to finish the calibration one next experimentally determines the quantities $S_{Au:Fe} - S_{Cu}$ and $S_{KP} - S_{Cu}$ by simply using a piece of high-purity copper as the sample. Figure 6 shows the relative

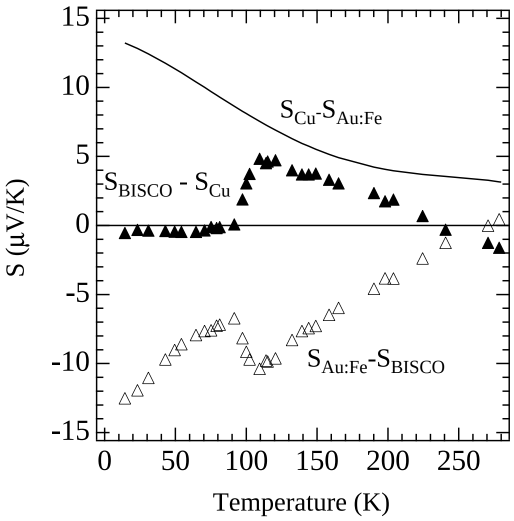

Figure 7. The experimentally determined thermoelectrical power of a superconducting sample $Bi_2Sr_2CaCu_2O_{7+\delta}$ (BISCO, $T_c \approx 95$ K).

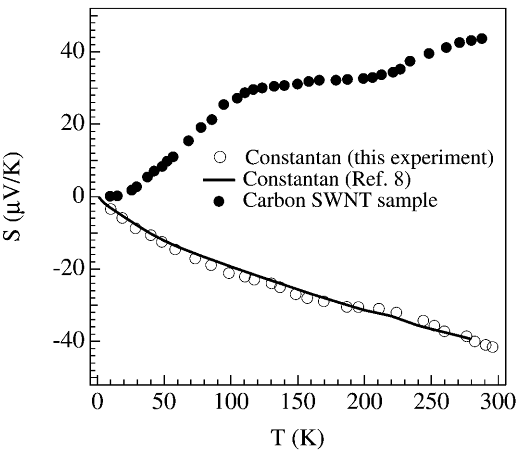

Figure 8. Experimental thermoelectrical power data for constantan and single-walled nanotube (SWNT) bundles of carbon. Data for constantan from [8] are shown (full curve) for comparison.

thermopowers of KP and Au:Fe with respect to copper, measured according to the above-mentioned method. Full curves represent the polynomial fits to each data set. To compute the absolute thermopower of the sample, the relative thermopowers are added, i.e., $(S_U - S_A) + (S_A - S_{Cu}) = S_U - S_{Cu}$. Then, tabulated values of S_{Cu} can be used to obtain S_U. It should be recalled that $|S_{Cu}| \lesssim 2\mu$ V K^{-1} over the range 4–300 K and therefore data on samples with large thermopowers are often reported as the relative thermopower $S_U - S_{Cu}$.

In figure 7, we show thermopower data for a superconducting polycrystalline pellet of $Bi_2Sr_2CaCu_2O_{7+\delta}$ ($T_c \approx 95$ K). The empty triangles are the sample thermopower with respect to Au:Fe, the full curve is the calibrated curve of the thermopower of Au:Fe against copper and the solid triangles represent the absolute thermopower of the sample. This measurement of a superconductor also allows one to verify the absolute zero of the sample thermopower below T_c.

In figure 8, we show typical data taken for two samples, one with high thermal conductivity (constantan) and one with relatively low thermal conductivity (a tangled mat of single-walled carbon nanotubes [9, 10]). It can be seen that, by using this technique, one can measure the thermoelectrical powers of samples with a wide range of thermal conductivities. For comparison, we have shown data for constantan obtained from [8].

It is also worth mentioning that, since

$$slope_A - slope_B = -1/g \qquad (8)$$

one can choose either of the outputs Y_A and Y_B to accumulate data with the best signal-to-noise ratio. It should also be noted that the least-squares fit of Y_A (Y_B) versus X to a straight line, which is routinely done via the computer to obtain each data point, provides an effective means for noise rejection. To emphasize the contribution due to the sample S_U in the relative thermopower, we usually choose Y_A (Au:Fe) for $T > 80$ K and Y_B (KP) for $T < 80$ K.

Acknowledgments

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