A new technique to obtain a fast thermocouple sensor for thermal diffusivity measurements in an extended temperature range

CALZONA, V., et al.

Abstract

An improved ac method to measure the thermal diffusivity in an extended temperature range is presented. The basic idea is to solder thermocouple wires directly on the sample, so that the sample itself acts as a thermocouple junction and the relaxation time for the temperature measurement becomes negligible. This new technique allows one to measure smaller samples and to increase the frequency of measurement so that the thermal losses could in principle be completely neglected. Finally, by the particular geometry a concurrent measurement of the electrical resistivity is obtained.

Reference


DOI: 10.1063/1.1144237

Available at:
http://archive-ouverte.unige.ch/unige:98447

Disclaimer: layout of this document may differ from the published version.
A new technique to obtain a fast thermocouple sensor for thermal diffusivity measurements in an extended temperature range

V. Calzona, M. R. Cimberle, C. Ferdeghini, G. Grasso, M. Putti, and A. S. Siri

Citation: Review of Scientific Instruments 64, 3612 (1993); doi: 10.1063/1.1144237
View online: http://dx.doi.org/10.1063/1.1144237
View Table of Contents: http://aip.scitation.org/toc/rsi/64/12
Published by the American Institute of Physics
A new technique to obtain a fast thermocouple sensor for thermal diffusivity measurements in an extended temperature range

V. Calzona, M. R. Cimberle, C. Ferdeghini, G. Grasso, M. Putti, and A. S. Siri
INFN, CNR, Dipartimento di Fisica, Via Dodecaneso 33, 16146 Genova, Italy

(Received 18 January 1993; accepted for publication 25 July 1993)

An improved ac method to measure the thermal diffusivity in an extended temperature range is presented. The basic idea is to solder thermocouple wires directly on the sample, so that the sample itself acts as a thermocouple junction and the relaxation time for the temperature measurement becomes negligible. This new technique allows one to measure smaller samples and to increase the frequency of measurement so that the thermal losses could in principle be completely neglected. Finally, by the particular geometry a concurrent measurement of the electrical resistivity is obtained.

I. INTRODUCTION

Thermal transport properties provide information about the interaction mechanisms of the heat carriers. This information could be of fundamental importance in systems such as high temperature superconductors where the nature of the carriers and their interactions are not yet clear. Nevertheless, in the high temperature range, because of the high thermal resistance of these materials, thermal losses can strongly affect thermal conductivity measurements and therefore reliable data above 200 K are not easily available.

In order to minimize the contribution of the heat losses, we developed an ac technique to measure in an extended range of temperature the thermal diffusivity (defined as the ratio between the thermal conductivity and the specific heat per unit volume). We verified that the small measurement time \( \Delta t = 1/f \approx 5-50 \) s limits the contribution of the heat losses. On the other hand the major problem was a thermocouple relaxation time not negligible with respect to the measurement time. In this paper we describe how this technique has been improved by drastically reducing the thermocouple response time.

The innovative idea is to solder, directly on the sample, wires of a selected material, [Au(Fe) in our case]. In this way the thermal sensor was the junction between the sample and the wire which measures directly the temperature of the sample itself. Clearly this kind of thermocouple is not easy to calibrate, but we will see that with the geometrical configuration we used we do not need to know temperatures or temperature differences, but only temperature ratios. We will show that no effect due to the thermal response of the thermocouple was observed at the highest frequency. Moreover, with wire soldering it is possible both to better define the sample positions where the temperature is measured and also to measure smaller samples, as single crystals. Consequently, this technique also works at high frequencies and allows one to neglect heat losses, at least below high temperatures. Finally, the soldered wires allow a concurrent four-wire resistivity measurement on the sample itself. Thermal diffusivity and electrical resistivity being both transport properties, are related; as the high-temperature superconductor can be affected by aging, it is important to have the possibility to perform both measurements on the same sample without changing the sample holder and the contacts.

II. PRINCIPLE OF MEASUREMENT

We consider the geometrical configuration, sketched in Fig. 1, in which a sample is fitted on a platform. \( T_1 \) is the temperature on the top of the sample and \( T_2 \) and \( T_3 \) are the temperatures in two points at distance \( d_1 \) and \( d_2 \), respectively, from the top of the sample. When sinusoidal pulses of heat, with frequency \( \omega = 2\pi f \) are supplied to the sample, stationary heat waves propagate into the sample and the solution of the one-dimensional heat equation gives

\[
\frac{T_1(\omega)}{T_1(\omega)} = \cosh[(\omega + \mu_i) \tau_i]^{1/2},
\]

where \( \tau_i = d_1^2/D \) is the relaxation time of a portion of the sample of length \( d_1 \) and thermal diffusivity \( D_i \); \( \mu_i \) is the heat loss rate taking into account the heat losses from the lateral and top surface of the portion \( d_1 \). By using the relationship \( (1) \) we obtain the equation

\[
R(\omega) = \frac{T_3(\omega) - T_1(\omega)}{T_2(\omega) - T_1(\omega)} = \frac{\cosh(i\omega \tau_2)^{1/2} - 1}{\cosh(i\omega \tau_1)^{1/2} - 1},
\]

where we suppose the frequency high enough to neglect the \( \mu_i \) coefficients. If we have the ideal configuration \( d_2 = 2d_1 \), Eq. (2) becomes

\[
R(\omega) = \frac{2[\cosh(i\omega \tau_1)^{1/2} + 1]}{\cosh(i\omega \tau_1)^{1/2} + 1},
\]

where \( \tau = d_1^2/D \). From this equation we can evaluate the thermal diffusivity \( D \). Following Ref. 2 we define \( \tau_i \) and \( \tau_1 \) as

\[
\tau_1 = \frac{2}{\omega} \text{Re} \left[ \cosh^{-1} \left( \frac{R(\omega)}{2} - 1 \right) \right],
\]

\[
\tau_2 = \frac{2}{\omega} \text{Im} \left[ \cosh^{-1} \left( \frac{R(\omega)}{2} - 1 \right) \right],
\]

and the thermal diffusivity is given by

\[
D = d_1^2/\tau = d_1^2/\sqrt{\tau_1 \cdot \tau_2},
\]
where $\tau = \tau = \tau$ because we neglected the heat losses.

In the more general case, $d_2 = 2d_1$, and thermal diffusivity cannot be analytically calculated from Eq. (2). Putting $d_2 = 2d$ and $d_1 = d - \delta$, Eq. (2) becomes

$$R(\omega) = \frac{\cosh[2(\omega r\tau)^{1/2} - 1]}{\cosh[(1 - \epsilon)(\omega r\tau)^{1/2} - 1]},$$

with $\epsilon = \delta/d$. If we assume $|\epsilon| \ll 1$, we can evaluate the error we made in calculating $D$ using Eq. (4) instead of the correct Eq. (5).

Figures 2(a) and 2(b) show, respectively, $|R(\omega)|$ and $\arg[R(\omega)]$ as a function of $\omega r\tau$ for $\epsilon = 0, 0.1, 0.2$. $|R(\omega)|$ increases exponentially with $\omega r\tau$ and it assumes higher values with increasing $\epsilon$. In particular when $\omega r\tau$ tends to zero $|R(\omega)| \approx 4(1 + 2\epsilon)$. Instead $\arg[R(\omega)]$ is a roughly linear function of $\omega r\tau$ and depends to a slight extent on $\epsilon$.

From Figs. 2(a) and 2(b) we can evaluate the $\omega r\tau$ range where $\tau$ can be measured with the greatest sensitivity. For $\omega r\tau < 1$, $R(\omega)$ is nearly constant and therefore independent of $\tau$. For $\omega r\tau > 10$, $R(\omega) > 10$ too. This means that $T_2 - T_1 < 0.1(T_3 - T_1)$ while the best experimental condition is when $(T_2 - T_1)$ does not differ too much from $(T_3 - T_1)$. We consider the optimal range to be $3 < \omega r\tau < 5$. So the frequency must be chosen depending on the $\tau$ value.

Figure 2(c) shows $\tau_r$ and $\tau_i$ vs $\omega r\tau$ as obtained, respectively, by Eqs. (4a) and (4b) for $r = 4$ and $\epsilon = 0, 0.1, 0.2$. As expected, for $\epsilon = 0$, $\tau_r = \tau_i = \tau$. For $\epsilon \neq 0$, $\tau_r$ and $\tau_i$ tend to the same value when $\omega r\tau$ increases and diverge almost symmetrically from this value when $\omega r\tau$ tends to zero. Figure 2(d) shows the geometrical mean $(\tau_r \cdot \tau_i)^{1/2}$ vs $\omega r\tau$. As $\epsilon$ increases, $(\tau_r \cdot \tau_i)^{1/2}$ departs from $\tau$, but it remains nearly constant across the whole $\omega r\tau$ range considered.

These results become evident if we consider, for $|\epsilon| \ll 1$, the first order Taylor expansion of

$$\cosh^{-1}\left(\frac{R(\omega)}{2} - 1\right) \approx (i\omega r\tau)^{1/2}\left[1 + \frac{\cosh(i\omega r\tau)^{1/2} + 1}{\cosh(i\omega r\tau)^{1/2} - 1}\right]$$

$$\approx (1 + i)(\omega r\tau/2)^{1/2}$$

$$\times \left[1 + \frac{\cosh(i\omega r\tau)^{1/2} + 1}{\cosh(i\omega r\tau)^{1/2} - 1}\right].$$

If we insert this expansion in Eqs. (4a) and (4b), it is
FIG. 3. Thermopower of Au(Fe0.07%) as a function of the temperature. The data was obtained by measuring the thermopower of the Au(Fe0.07%).Pb thermocouple with $S_{th}$ reported in Ref. 3.

evident that, for $\epsilon \neq 0$, $r_\tau$ and $\tau_\tau$ diverge at low frequencies, whilst at high frequency ($\omega \tau > 1$) they converge to $\tau(1 + 2\epsilon)$.

This last behavior is shown in Fig. 2(d); the quantity $(\tau_\tau - \tau_\tau)^{1/2}$ remains nearly constant in the $\omega \tau$ range suitable for thermal diffusivity measurements. So we will assume that, for $|\epsilon| < 1$:

$$ (\tau_\tau - \tau_\tau)^{1/2} \approx \tau(1 + 2\epsilon) = d^2 / \rho(1 + 2\epsilon). \quad (6) $$

If $d$ and $\epsilon$ are known, we can use this equation to calculate the thermal diffusivity.

We point out that Eq. (6) is independent of frequency because the contribution of heat losses and the presence of thermometer relaxation time were neglected.

III. EXPERIMENT

Experimental details regarding the cryostat and the magnet description, the instrumentation and the automation procedure have been provided elsewhere. In this section we will describe how the sample was adjusted to allow thermal diffusivity and electrical resistivity measurements.

Three Au(0.07%Fe) wires were soldered on the sample using silver paint. Wire 1 is soldered on the top of the sample and wires 2 and 3 are soldered at distance $d_1$ and $d_2$, respectively, from the top of the sample with $d_2 = 2d_1$. The sample itself is soldered on a copper platform which is electrically insulated from the cryostat.

In the thermal diffusivity measurements the voltage differences $(V_2 - V_1)$ and $(V_3 - V_1)$ are measured. The voltage differences

$$ (V_2 - V_1) = (S_w - S_s)(T_2 - T_1) $$

are proportional to the temperature differences, where $S_w$ and $S_s$ are the thermoelectric powers of the wires and of the sample, respectively. The thermoelectric power of the Au(0.07%Fe) wires is shown in Fig. 3. The thermoelectric power of the sample is generally unknown but the technique we have used does not require us to know temperature differences but only a ratio between temperature differences. In fact the ratio $R$:

$$ R = \frac{T_3 - T_1}{T_2 - T_1} = \frac{V_3 - V_1}{V_2 - V_1} $$

does not depend on thermoelectric powers.

On the other hand, the knowledge of the sign, and of the order of magnitude of $S_s$ is important in choosing the wire material, because the sensitivity of the measurement obviously depends on $(S_w - S_s)$. For example, to measure a YBaCuO sample we have to consider that its thermoelectric power is a few mV/K (positive or negative depending on the oxygen content) decreasing with the temperature. Au(Fe) wires is a good choice for low temperature measurements (below 100 K). At high temperatures a better choice could be Chromium wires, with a thermopower increasing with temperature up to 20 mV/K at 300 K.

We should stress here that our technique is not limited to the measurement of metallic samples. In fact the thermocouples can also be made by evaporating on a nonconducting sample a suitable metal layer on which the wires can be soldered.

The resistivity measurements are performed by the standard four wires method. By feeding current between the platform, electrically connected to the sample, and the wire on the top of the sample, the resistivity can be known by measuring the voltage difference $(V_3 - V_2)$.

Thermal diffusivity is measured with increasing temperature using the automated procedure described in Ref. 2. Typically, resistivity is measured during the cool down by feeding low frequency (0.1–0.5 Hz) ac current so that the instrumentation and the automation procedure used for thermal diffusivity measurements are maintained.

IV. MEASUREMENT OF A YBaCuO SAMPLE

To check the reliability of the method and the frequency range where it works, thermal diffusivity measurements were performed at fixed temperatures and varying frequencies. We present data acquired at a high temperature ($T = 303$ K), where high thermal losses and long thermocouple relaxation time could further limit the range of frequency available for the measurement. We measured a YBa$_2$Cu$_3$O$_y$ sintered sample 5.6-mm long, with a cross section of $2 \times 2.8$ mm$^2$. Distances $d_1 = 2.0.05$ mm and $d_2 = 4.4 \pm 0.05$ mm were accurately measured with an optical microscope and the indetermination depended only on the dimension of the soldering. So we had $d = d_2 / 2 = 2.2 \pm 0.025$ mm and $\epsilon = (d_2 - d_1) / d = 0.09 \pm 0.03$.

Figures 4(a)–4(d) show the experimental values of $|R(\omega)|$, $\arg[R(\omega)]$, $r_\tau$, and $\tau_\tau$, respectively as a function of the frequency $f$ at $T = 303$ K. The continuous curves are obtained by introducing $\epsilon$ in Eq. (5) and varying $\tau$ in order to best fit the experimental data. Such procedure was performed for frequencies higher than 0.06 Hz to avoid a possible heat loss contribution.

The theoretical curves reproduce the experimental ones fairly well using only one parameter. In Fig. 4(a) we observed that at low frequency $|R(\omega)|$ tends to 4.9, in accord with the expected value $|R(0)| = 4(1 + 2\epsilon) = 4.72 \pm 0.24$. 

$max$ thermocouple sensor
FIG. 4. (a) \(|R(f)|\) vs \(f\); (b) \(\arg[R(f)]\) vs \(f\); (c) \(\tau_r\) and \(\tau_i\) vs \(f\); (d) \((\tau_r \cdot \tau_i)^{1/2}\) vs \(f\). The symbols represent measurements on a \(\text{YBa}_2\text{Cu}_3\text{O}_7\) sintered sample at \(T=303\) K. The continuous curves are obtained by relation (5) with \(\varepsilon=0.09\) and \(\tau=3.4\).

The thermal diffusivity measurements were performed between 90 and 330 K. \(D\) was simultaneously measured at two frequencies (see Ref. 2) and the values obtained, as predicted by Eq. (6), were independent of frequency. During the measurements the frequency was varied proportionally to \(D\) (see Ref. 2) so that \(\omega r\) was kept constant at 3.5. Electron contribution to thermal diffusivity, defined as

\[ D_e(T) = \frac{K_e(T)}{C(T)} \]

is shown in Fig. 5, where \(K_e(T)\) is evaluated by the Wiedemann–Franz law, \(K_e(T) = L_0 T / \rho(T)\) with \(L_0=2.45 \times 10^{-8}\) W·Ω·K\(^{-2}\) and \(\rho(T)\) is measured between 90 and 280 K; \(C(T)\) is the specific heat per unit volume obtained by Ref. 6. We obtained \(D_e\) one order of magnitude lower than \(D\), which is in line with typical results for \(\text{YBa}_2\text{Cu}_3\text{O}_7\) sintered samples.\(^1\)
V. DISCUSSION

At the moment our technique is limited by the use of commercial nanovoltmeters which do not allow high frequency measurements. This problem can be overcome, so it is worth analyzing the perspectives of this method.

Moreover the sample-wire soldering, as in resistivity measurements, can be miniaturized to allow measurements on small single crystals. When the distance decreases, the relaxation time decreases with $d^2$ [Eq. (4c)]. As a consequence, to have $\omega \tau > 1$, the frequency must be increased. For example, if we consider a YBa$_2$Cu$_3$O$_7$ single crystal at low temperature with thermal diffusivity ten times higher and $d$ four times shorter than for a sintered sample, $\tau$ could be $10^{-2}$–$10^{-1}$ s and the measurement frequency would have to be higher than 2–20 Hz. In any case we would expect the sample-wire thermocouple to work at such frequencies since the thermoelectric power is an electron property whose characteristic frequencies are much higher.

The possibility to work at such a high frequency allowed us to neglect thermal losses completely, so the technique could be suitable for measuring thermal diffusivity at very high temperatures (400–600 K). Clearly, no method using a glued thermometer can reach such high temperatures.

Finally, we verified the frequency independence of our methodology by at least a decade around the measurement frequency. This capability makes it possible to use the frequency as a parameter, so we suggest this technique for studying systems, such as glasses, spin glasses, and systems near phase transition, where thermal properties depend on time.

ACKNOWLEDGMENTS

This work was partially supported by INFM and by C.N.R. under the “Superconductive and Cryogenic Technologies” project.