

# On the piezoelectric contribution to the photopyroelectric signal

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(Received 19 October 2004; accepted 25 December 2004; published online 15 February 2005)

The most important goal of the photopyroelectric (PPE) technique, wherein an opaque sample is periodically illuminated on one face while the other is in contact with the pyroelectric detector, is its ability to measure the thermal properties across phase transitions with high accuracy. For thermally thick samples, the logarithm of the amplitude and the phase of the PPE signal are parallel straight lines when represented as a function of the square root of the modulation frequency. From their slope and from their vertical separation, thermal diffusivity and thermal effusivity are obtained, respectively. However, these linear relations are lost when measuring solid samples below 230 K, the temperature at which the coupling fluid used to guarantee the thermal coupling between the sample and the pyroelectric detector freezes. In this work we demonstrate quantitatively that this loss of linearity is due to the piezoelectric contribution to the pyroelectric signal, which increases with the stiffness of the coupling fluid. Moreover, a multiparametric fitting allows us to retrieve the thermal parameters. © 2005 American Institute of Physics. [DOI: 10.1063/1.1865772]

## I. INTRODUCTION

The photopyroelectric technique (PPE) has been widely used to measure the thermal properties of solids and liquids (see Ref. 1 and references therein). In the standard back configuration, where an opaque sample is periodically illuminated on one side while the other side is in contact with the pyroelectric detector, the thermal parameters can be obtained from simple linear relations. For thermally thick samples, the natural logarithm of the amplitude and the phase of the PPE signal are parallel straight lines when represented as a function of the square root of the modulation frequency. From their slope and from the vertical separation, thermal diffusivity ( $D$ ) and thermal effusivity ( $e = \sqrt{\rho c K}$ ) are obtained, respectively. From the constitutive relation ( $K = \rho c D$ , where  $\rho$  is the density), thermal conductivity ( $K$ ), and specific heat ( $c$ ) can then be retrieved.<sup>2,3</sup> Moreover, their temperature dependence can be obtained from one single heating and/or cooling run at a fixed frequency. That is why the PPE technique is especially suited to study phase transitions.<sup>4</sup>

However, in spite of its high resolution, some drawbacks appear when working with solid materials. Unlike when measuring fluid samples (liquid crystals, oils, food stuffs, etc.), a coupling fluid layer (silicone grease or similar) must be used to guarantee the thermal coupling between solid samples and the pyroelectric detector. Although being extremely thin (only a few microns), it introduces some difficulty. On the one hand, the effect of the grease layer is to increase the slope of the above-mentioned linear relations, and therefore the thermal diffusivity of the solid under study is always undervalued.<sup>5</sup> On the other hand, at temperatures below about 230 K, at which the fluid layer freezes, the linear relations are dramatically distorted, especially at high

frequencies. The origin of that distortion is related to the fact that the pyroelectric detector is also piezoelectric. While the grease remains fluid, the mechanical coupling is small enough to prevent the thermal strains induced in the sample by the thermal wave from being transmitted to the detector, and therefore only a pure pyroelectric voltage is recorded. However, when the grease freezes, it becomes very stiff and transmits very well the thermal strains to the detector; consequently, a piezoelectric voltage is generated together with the pyroelectric one.

The aim of this work is to account for this piezoelectric contribution. In this way, we demonstrate that it is responsible for the distortion of the linear relations of the PPE signal. Moreover, by fitting the experimental data to this superimposed pyroelectric and piezoelectric voltage, the thermal diffusivity and effusivity of solid samples down to 77 K are obtained accurately.

## II. THEORY

The geometry of the problem we are dealing with is shown in Fig. 1. In it,  $g$ ,  $s$ , and  $p$  stand for the gas, sample, and pyroelectric detector, respectively. We assume an opaque sample whose surface is illuminated by a defocused light beam modulated at a frequency  $f$ . If the sample and the pyroelectric detector are both thermally thick (e.g., their thickness  $L$  is higher than the thermal diffusion length) the pyroelectric voltage is given by<sup>1</sup>

$$V_{py} = AF \frac{I_0(1-R_s)}{K_s} \frac{1}{\sigma_p \sigma_s} \frac{e_s}{e_s + e_p} \exp(-\sigma_s L_s), \quad (1)$$

where  $I_0$  is the light beam intensity,  $R$  is the optical reflection coefficient, and  $\sigma = (1+i)/\mu$ , where  $\mu = \sqrt{D/\pi f}$  is the thermal diffusion length.  $A$  is a frequency-independent factor that depends on the physical properties of the detector (pyroelectric coefficient, thickness, dielectric constant, and permittivity).

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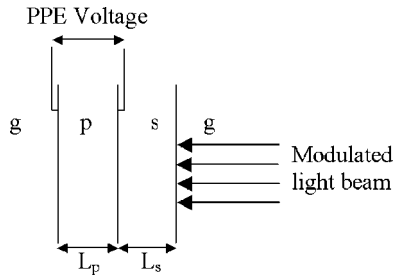


FIG. 1. Geometry of the problem.

ity). On the other hand,  $F$  is a frequency-dependent factor that accounts for the influence of the detection electronics.

For normalization purposes, we take into consideration the pyroelectric voltage produced by the pyroelectric detector in the absence of the sample:

$$V_{\text{pyro}} = AF \frac{I_0(1-R_p)}{2K_p} \frac{1}{\sigma_p^2}. \quad (2)$$

To calculate the piezoelectric voltage, we follow the approach used by Blonskij and co-workers.<sup>6</sup> This method is restricted to low modulation frequencies, for which the thermoelastic strains in the sample are quasistatic and the generation of acoustic waves is neglected. On the other hand, as the thermal waves are highly damped, only the thermoelastic strains generated inside the sample are considered, and they are not influenced by the presence of the detector. In the case of a thermally thick sample, the piezoelectric voltage is given by<sup>6</sup>

$$V_{\text{pz}} = -BF \frac{I_0(1-R_s)}{K_s} \frac{1}{\sigma_s^2 L_s} \left(1 - \frac{3}{\sigma_s L_s}\right), \quad (3)$$

where  $B$  is a constant depending on the physical properties of the detector (piezoelectric coefficients, dielectric constant, surface, and thickness) and on the thermal expansion coefficient of the sample.

The resultant voltage is the sum of both pyroelectric and piezoelectric contributions:  $V = V_{\text{py}} + V_{\text{pz}}$ . If we normalize by dividing this total voltage by the voltage provided by the bare detector as given by Eq. (2), we obtain

$$V_n = \left( \frac{1-R_s}{1-R_p} \right) \frac{2e_p}{e_s + e_p} \exp(-\sigma_s L_s) - C \left( \frac{1-R_s}{1-R_p} \right) \frac{\sqrt{D_s}}{e_s L_s} \left(1 - \frac{3}{\sigma_s L_s}\right), \quad (4)$$

where the first term represents the pyroelectric contribution, which dominates at low frequencies, and the second one the piezoelectric contribution, which dominates at high frequencies where thermal waves vanish. Here the frequency-independent  $C = 2BK_p/AD_p$  measures the relative intensity of the piezoelectric effect with respect to the pyroelectric one.

To estimate the influence of the piezoelectric contribution to the PPE signal, we have evaluated Eq. (4) using the following parameters:  $D_s = 1 \text{ mm}^2/\text{s}$ ,  $e_s = 3000 \text{ W m}^{-2} \text{ K}^{-1} \text{ s}^{1/2}$ ,  $L_s = 0.5 \text{ mm}$ ,  $e_p = 3700 \text{ W m}^{-2} \text{ K}^{-1} \text{ s}^{1/2}$ ,  $R_s = 0.1$ , and  $R_p = 0.82$ . The behavior of the natural logarithm of the amplitude  $\ln(V_n)$  and of the phase  $\Psi_n$  as a

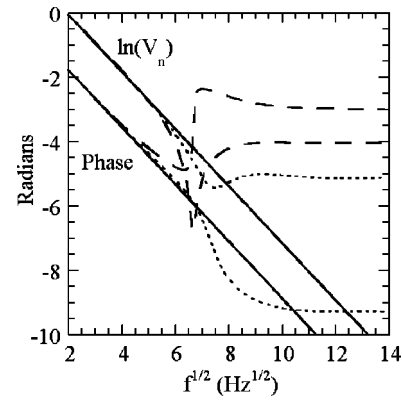


FIG. 2. Theoretical calculations of the frequency dependence of the PPE amplitude and phase. The continuous line represents the pure pyroelectric behavior, the dotted line the influence of a weak piezoelectric effect and the dashed line the influence of a strong piezoelectric effect.

function of  $\sqrt{f}$  is shown in Fig. 2. Three values of  $C$  have been considered: 0, 2, and 6. For  $C=0$  [continuous line], the pure pyroelectric behavior is found, where  $\ln(V_n)$  and  $\Psi_n$  are parallel straight lines. From their slope  $m$  and from the vertical separation  $\Delta$ , the thermal diffusivity and the thermal effusivity of the sample can be obtained:<sup>1,5</sup>

$$D_s = \pi L_s^2 / m^2 \quad \text{and} \quad e_s = e_p \left( \frac{2 \left( \frac{1-R_s}{1-R_p} \right)}{e^\Delta} - 1 \right).$$

For  $C \neq 0$ , the piezoelectric contribution modifies the high-frequency tails in such a way that  $\ln(V_n)$  and  $\Psi_n$  asymptotically approach a constant value. However, a significant difference is found depending on the strength of the piezoelectric contribution: If it is weak ( $C=2$ , dotted line) the phase converges to  $-3\pi$ , while if it is strong ( $C=6$ , dashed line) the phase approaches  $-\pi$ . In this example, the limiting value for which the phase tends to approach  $-3\pi$  is  $C \approx 5$ .

It is worth noting that a similar modification of the linear behavior arises when a small amount of the modulated heating light beam reaches the pyroelectric detector. The effect of this parasitic light in the PPE signal is accounted for by the addition of a real and frequency-independent term to the pure PPE voltage [first term in Eq. (4)]. Although the shape of  $\ln(V_n)$  and  $\Psi_n$  is very similar to that shown in Fig. 2, at high frequencies the phase converges to 0 (for strong parasitic light) or to  $-2\pi$  (for weak parasitic light). In this way, we can distinguish easily between both effects.

The combined pyroelectric and piezoelectric effects was proposed by Aravind and Fung to measure the thermal diffusivity of Si samples.<sup>7,8</sup> However, they used the low-frequency range where the sample changes from thermally thin to thick, and therefore they did not find the dramatic modification of the linearity that is shown in Fig. 2.

### III. EXPERIMENTAL RESULTS AND DISCUSSION

A conventional PPE setup in the standard back configuration<sup>1</sup> has been used to verify the validity of the model about the piezoelectric contribution to the photopyroelectric signal developed in the previous section. A mechanically modulated He-Ne laser beam of 5 mW illuminates the

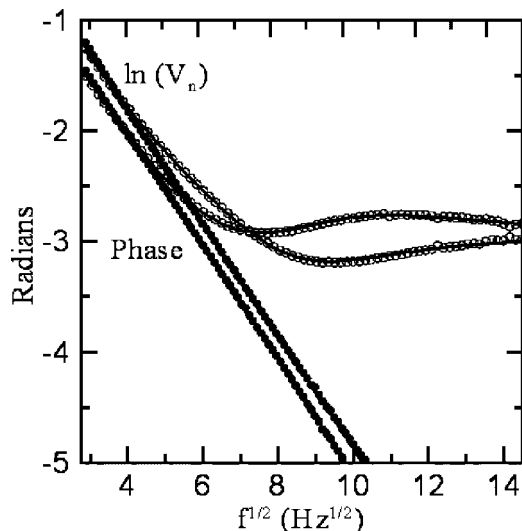


FIG. 3. Frequency scans of the PPE amplitude and phase in a  $\text{Cr}_2\text{O}_3$  sample 0.528 mm thick at 300 K. Dots are the experimental data using silicone grease as coupling fluid. Open circles are the experimental data using silver paint. The continuous line is the best fitting to Eq. (4).

upper surface of the sample under study. Its rear surface is in thermal contact with a 350- $\mu\text{m}$ -thick Z-cut  $\text{LiTaO}_3$  pyroelectric detector using a very thin layer of high vacuum silicone grease. This detector is glued to the sample holder of a nitrogen bath cryostat that works between 77 and 500 K. The signal from the detector is directly analyzed by a lock-in amplifier in the current mode. The advantages of using a current preamplifier instead of a high impedance voltage preamplifier have been studied by Chirtoc and co-workers.<sup>9</sup> It is worth noting that the same Eq. (4) is valid for the normalized PPE voltage and for the normalized PPE intensity. This is due to the fact that the instrumental transfer function, that incorporates the effect of the electronic circuitry, is cancelled by normalization to the bare detector. That is why, in the remainder of this article, we will refer to the normalized PPE voltage  $V_n$ , although we really record the PPE intensity.

A frequency scan of the normalized PPE signal of a  $\text{Cr}_2\text{O}_3$  single crystal 0.528 mm thick performed at 300 K is shown by filled circles in Fig. 3. As can be seen, the linearity and parallelism of both amplitude and phase are very good in a wide frequency range, as predicted by the pure pyroelectric model. No feature of the piezoelectric contribution appears. From their slopes we obtain a thermal diffusivity value of  $3.36 \pm 0.12 \text{ mm}^2/\text{s}$  and a thermal effusivity of  $8200 \pm 500 \text{ W m}^{-2} \text{ K}^{-1} \text{ s}^{1/2}$ . These values are in good agreement with those reported by Marinelli and co-workers using a similar PPE device:<sup>10</sup>  $D_s = 3.3 \text{ mm}^2/\text{s}$  and  $e_s = 8400 \text{ W m}^{-2} \text{ K}^{-1} \text{ s}^{1/2}$ . The uncertainty of this last value is related mainly to the determination of the optical reflection coefficients of sample and detector. We then repeated the same frequency scan after changing the silicone grease used as coupling fluid for a small drop of silver paint, which after several minutes solidifies. The results are plotted by open circles in Fig. 3, showing a clear deviation from the linear behavior, which qualitatively resemble the theoretical predictions of Fig. 2 for the case of a strong piezoelectric effect. The multiparametric fitting to Eq. (4), with  $D_s$ ,  $e_s$ , and  $C$  as

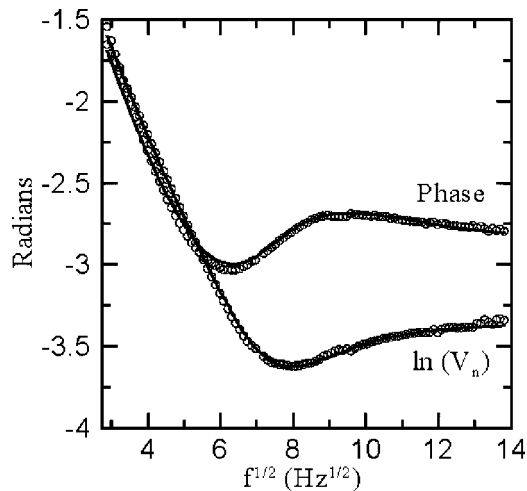


FIG. 4. Frequency scans of the PPE amplitude and phase in a  $\text{LaMnO}_3$  sample 0.675 mm thick at 120 K. Open circles are the experimental data, and the continuous line is the best fit to Eq. (4).

free parameters, is plotted in Fig. 3 by a continuous line that fits very well the experimental data. The corresponding fitting parameters are  $D_s = 3.25 \pm 0.12 \text{ mm}^2/\text{s}$ ,  $e_s = 8700 \pm 500 \text{ W m}^{-2} \text{ K}^{-1} \text{ s}^{1/2}$ , and  $C = 92 \pm 3$  with a correlation parameter  $R = 0.995$ . This last  $D$  value is lower than the previous one since the silver paint layer is thicker than the silicone grease. From these results two conclusions can be obtained. On one hand, it has been demonstrated that the piezoelectric effect is responsible for the breaking of the linear behavior of the frequency scans when the coupling fluid becomes very stiff. Moreover, and what is more interesting from an applications point of view, the thermal parameters ( $D$  and  $e$ ) can be obtained from a model fitting.

In the last years, we have been studying the thermal properties of perovskite manganites of the type  $\text{Ln}_{1-x}\text{A}_x\text{MnO}_3$ , where Ln is a lanthanide and A an alkaline earth, close to their magnetic phase transition. These materials are interesting because they show colossal magnetoresistance (a huge reduction in the electrical resistivity by the application of a magnetic field). In particular, the undoped  $\text{LaMnO}_3$  has an antiferromagnetic to paramagnetic phase transition at about 137 K. In Fig. 4 we show by open circles a frequency scan performed on a  $\text{LaMnO}_3$  sample 0.675 mm thick at 120 K. Even though silicone grease was used as coupling fluid, the amplitude and phase of the PPE signal are influenced by the piezoelectric effect. This is due to the fact that silicone grease freezes below about 230 K. This means that below this temperature limit, the linear method cannot be used to measure the thermal properties. However, by fitting these experimental data to Eq. (4) (see the continuous line in Fig. 4) we obtain  $D = 3.51 \pm 0.13 \text{ mm}^2/\text{s}$ ,  $e = 4100 \pm 300 \text{ W m}^{-2} \text{ K}^{-1} \text{ s}^{1/2}$ , and  $C = 54 \pm 2$  with a correlation parameter  $R = 0.995$ .

Similar agreement between experimental data and Eq. (4) has been found whenever a frequency scan below 230 K has been carried out. Measurements performed on a wide variety of materials confirm that the piezoelectric effect is the responsible for the deviation from linearity of the frequency scans, and that this contribution to the pyroelectric

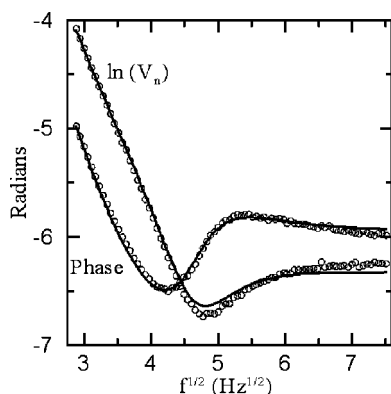


FIG. 5. Frequency scans of the PPE amplitude and phase in a  $\text{Sn}_2\text{P}_2\text{S}_6$  sample 0.429 mm thick at 300 K. Open circles are the experimental data, while the continuous line is the best fit to Eq. (4).

signal is governed by the simple expression of Eq. (3). Only an anomalous result deserves comment. This is the case of  $\text{Sn}_2\text{P}_2\text{S}_6$ , a ferroelectric material that undergoes a transition to the paraelectric state at 337 K. A frequency scan of a 0.429-mm-thick sample at 300 K is shown in Fig. 5. Although silicone grease was used as coupling fluid, the piezoelectric contribution is strong enough to distort the expected straight lines. The anomaly is related to the fact that the phase converges to  $-2\pi$  instead of to  $-\pi$ . The fitting of the experimental data to Eq. (4) gives a negative value of the constant  $C$ . Actually, by using negative values of  $C$  in Eq. (4), we can see that the phase converges to  $-4\pi$  or to  $-2\pi$  for weak and strong piezoelectric contributions, respectively. The physical meaning of this negative sign of  $C$  is related to the fact that this constant is proportional to the thermal expansion coefficient of the sample under study, and this is negative for this material below the transition temperature.<sup>11,12</sup>

All the experimental measurements have been performed using a  $\text{LiTaO}_3$  crystal as pyroelectric detector. However, we have also checked the influence of the piezoelectric effect when using a PZT ceramic as pyroelectric detector. Although PZT has a higher pyroelectric coefficient than  $\text{LiTaO}_3$ , the piezoelectric contribution is so high that even if the coupling fluid remains liquid the linear behavior of the amplitude and

phase is distorted as much as when using  $\text{LiTaO}_3$  with solidified silver paint as coupling medium. Therefore, we can conclude that  $\text{LiTaO}_3$  is a better choice than PZT for thermal measurements. Anyway, we are looking for other pyroelectric materials with very low piezoelectric coefficients as possible candidates to substitute  $\text{LiTaO}_3$ .

As a final conclusion, we can say that the piezoelectric effect greatly influences the PPE signal when the coupling layer used between the sample and the pyroelectric detector becomes very stiff. Moreover, this piezoelectric contribution is governed by a simple expression. Finally, by fitting the experimental data to the superimposed pyroelectric and piezoelectric signal, the thermal diffusivity and effusivity of solid samples in the temperature range from 230 to 77 K (where the linear method cannot be used) can be measured accurately.

## ACKNOWLEDGMENTS

This work has been supported by the Ministerio de Ciencia y Tecnología through Research Grant No. MAT2002-04153-C02-01 (50% FEDER funds).

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