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## Self consistently calibrated photopyroelectric calorimeter for the high resolution simultaneous absolute measurement of the specific heat and of the thermal conductivity

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High temperature resolution study of the specific heat and of the thermal conductivity over the smecticA-nematic and nematic-isotropic phase transitions in octylcynobiphenyl liquid crystal using a new photopyroelectric calorimetry configuration are reported, where, unlike previously adopted ones, no calibration is required other than the procedure used during the actual measurement. This makes photopyroelectric calorimetry suitable for “absolute” measurements of the thermal parameters like most other existing conventional calorimetric techniques where, however, the thermal conductivity cannot be measured. *Copyright 2012 Author(s). This article is distributed under a Creative Commons Attribution 3.0 Unported License.* [doi:10.1063/1.3684962]

The study of phase transitions by calorimetric measurements is a well established and useful practice since the heat capacity is related to the microscopic structure of condensed matter and plays an important role in monitoring the changes in the energy content of a system. In particular, in the vicinity of phase transitions, the specific heat can show an anomalous behaviour due to energy fluctuations, and it can show a frequency dependence because of relaxation phenomena of some energetic degrees of freedom over glass transitions. Thermal transport properties are also important in phase transition studies since they are very sensitive to the sample structure, composition and thermal history. Calorimetric measurements are thus of fundamental importance for characterizing many physical systems, particularly when performed by those techniques which enable the achievement of high temperature resolution results and which can operate over a large frequency range.

Photopyroelectric (PPE) calorimetry<sup>1</sup> is a high resolution a.c. technique which has been shown to meet all the above mentioned requirements. It enables frequency dependent measurements of the specific heat and, unlike other techniques, also of the thermal transport parameters over a very wide frequency range.<sup>2</sup> It allows also to correlate the thermal characterization with simultaneously performed polarization microscopy observations and with optical scattering measurements.<sup>3</sup> Finally it has been shown to be able to detect latent heat or other kind of enthalpy exchange over phase transitions.<sup>4</sup>

In most calorimetric techniques, among which Adiabatic Scanning Calorimetry,<sup>5</sup> Nonadiabatic Scanning Calorimetry,<sup>6</sup> *ac*-Calorimetry,<sup>7,8</sup> differential scanning calorimetry,<sup>9</sup> after some initial calibration procedure, the actual value of the thermal parameters can be obtained in any unknown sample. In the case of temperature dependent measurements of the thermal parameters by PPE calorimetry, it is required that the signal amplitude and phase be normalized to the respective values obtained at a temperature where the thermal parameters are known. This has made PPE, to date, a sort of “relative” calorimetric technique and may pose limitations to its use. So in the present work we present simultaneous measurements of the specific heat,  $c$ , and of the thermal conductivity,  $k$ , performed by a new “absolute” PPE calorimeter, where no calibration is necessary other than

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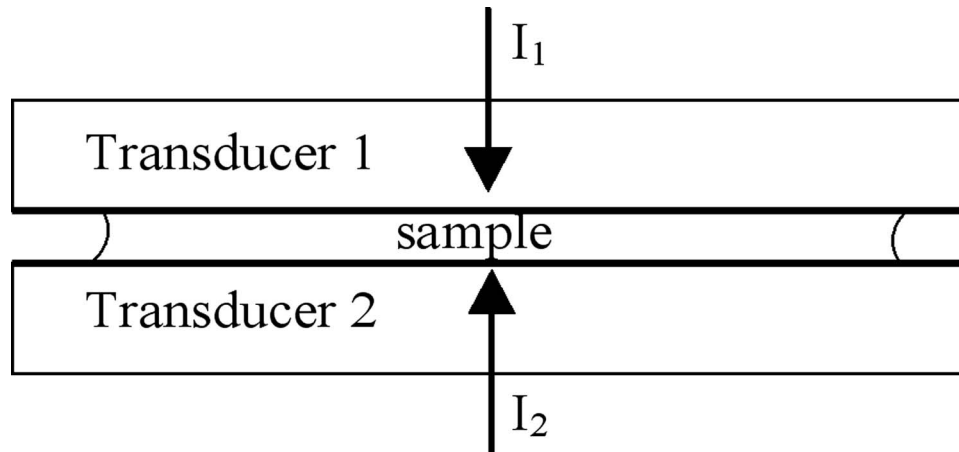


FIG. 1. Sketch of sample cell described in the text.

the procedure used during the actual measurement. We test the reliability of the obtained results against those of a particular kind of “standard” sample, namely octylecyanobiphenil (8CB) liquid crystal compound, where the values of  $c$  in particular, but also of  $k$ , are well known and have been repeatedly measured over the years by a variety of calorimetric techniques,<sup>10-12</sup> and where, due to the presence of phase transitions, both  $c$  and  $k$  present substantial variations with temperature. The detection and measurement of such known variations can constitute a convincing test of the reliability of the results. In short, instead of measuring several values of the thermal parameters in different standard samples at the same temperature, we present measurements on the same well known sample at several temperatures where the values of the thermal parameters may markedly differ. This approach is useful to test also the temperature resolution of the results granted by the technique, and, in particular, to establish whether such resolution is sufficient for the study of critical phenomena over phase transitions.<sup>5</sup> The reported measurements are thus those performed over the smecticA-nematic (AN) and nematic-isotropic (NI) phase transitions regions of 8CB liquid crystal.

Fig. 1 shows a sketch of the photopyroelectric cell. The sample is contained between two pyroelectric transducers coated with a transparent ITO electrode on one side and with Ti electrode on the opposite side neighbouring the sample. When, for example, beam 1 reaches the opaque Ti electrode, after having crossed the ITO layer and transducer 1, a front detection (FD) signal<sup>2,13</sup>  $F_1$ , is generated in transducer 1 and a rear detection (RD) signal,<sup>14</sup>  $R_2$ , in transducer 2. The opposite occurs when illuminating the system on the opposite side with beam 2, yielding, respectively,  $F_2$  and  $R_1$ .

When the sample and pyroelectric transducer thicknesses, respectively,  $L_s$  and  $L_p$ , are much larger than the optical penetration depths in the respective media (optically thick), and are larger than the corresponding thermal diffusion length,  $\mu_i = (\pi f / D_i)^{1/2}$  (thermally thick), where,  $i = s, p, f$  is the modulation frequency of the heating beam,  $D_i = k_i / \rho_i c_i$  is the thermal diffusivity, and  $k_i$ ,  $\rho_i$  and,  $c_i$  are, respectively, the thermal conductivity, the density and the specific heat in each medium, then the signal amplitude and phase in the RD configuration and in the voltage mode, read:<sup>1,14,15</sup>

$$|R| = F_E(f) \frac{pAI}{2L_p \rho_p c_p} \frac{2e^{-(L_s/\mu_s)}}{(1 + \frac{e_p}{e_s})(1 + \frac{e_s}{e_p})} \quad (1)$$

$$\phi_R = \varphi_E(f) - L_s/\mu_s \quad (2)$$

Here  $e_i = (k_i \rho_i c_i)^{1/2}$  is the thermal effusivity,  $I$  is the non reflected part of the heating beam intensity,  $p$  and  $A$  are, respectively, the transducer pyroelectric coefficient and area.  $F_{E(f)}$  and  $\varphi_E(f)$  represent, respectively, the electronic component of the signal amplitude and phase. They contain the low-pass filter terms of the detection equivalent circuit,<sup>15</sup> and possible additional frequency dependent terms associated with the detection electronics intrinsic response. Under the same conditions the FD signal

amplitude and phase read:<sup>2,16</sup>

$$|F| = F_E(f) \frac{pAI}{2L_p \rho_p c_p} \frac{1}{(1 + \frac{e_s}{e_p})} \quad (3)$$

$$\phi_F = \varphi_E(f) \quad (4)$$

Then if one calculates the amplitude and phase, for example, of the ratio of the signals  $\frac{R_2}{F_1}$  obtained when illuminating with beam 1, it yields:

$$\frac{|R_2|}{|F_1|} = A_{21} = M_{21}(f) \left[ 2e^{-\frac{L_s}{\mu_s}} / (1 + \frac{e_p}{e_s}) \right] \quad (5)$$

$$\phi_{R_2} - \phi_{F_1} = \Phi_{21} = \left[ -\frac{L_s}{\mu_s} \right] + \theta_{21}(f) \quad (6)$$

The terms between square brackets in (5) and (6),  $A_T$  and  $\phi_T$ , respectively, represent the parts of the signal amplitude and phase containing the sample thermal parameters and

$$M_{21}(f) = \frac{F_{E2}(f) p_2 A_2 L_{p1}}{F_{E1}(f) p_1 A_1 L_{p2}} \quad (7)$$

$$\theta_{21} = [\varphi_{E2}(f) - \varphi_{E1}(f)] \quad (8)$$

contain electronics and geometrical contributions. The indexes get reversed when illuminating with beam 2 to obtain  $\frac{R_1}{F_2}$ . Note that such signal ratios are independent of their corresponding heating beam intensity. Now, since  $M_{21}(f) = (M_{12}(f))^{-1}$  and  $\theta_{21}(f) = -\theta_{12}(f)$ , then we can determine:  $M_{21} = \sqrt{\frac{M_{21}}{M_{12}}} = \sqrt{\frac{A_{21}}{A_{12}}}$  and  $\theta_{21} = \frac{1}{2}(\theta_{21} - \theta_{12}) = \frac{1}{2}(\Phi_{21} - \Phi_{12})$  to calculate:  $A_T = \frac{A_{21}}{M_{21}}$  and  $\phi_T = \Phi_{21} - \theta_{21}(f)$ .

When the two pyroelectric transducers are made of the same material, have very similar geometry and are connected to very similar detection electronics then, as in our case,  $M_{21} \approx 1$  and  $\theta_{21} \approx 0$ . Moreover, and most important, since the temperature dependence of the terms at the numerator and denominator in eq. (7) is very similar, then  $M_{21}(f)$  is practically temperature independent, as verified in our measurements. Similar considerations apply to  $\theta_{21}$ . Therefore, no calibration is necessary for the temperature dependence of the transducer response, contained in the terms  $M_{21}$  and  $\theta_{21}$ , which need to be determined only at a single temperature. Consequently, only one set of front and rear detection signals, say  $R_2$  and  $F_1$ , need to be measured, at the operating frequency, as a function of temperature to determine  $A_T(T)$  and  $\phi_T(T)$ , and this can be done simultaneously using only the beam 1 illumination. In our set up the sample thickness  $L_s$  was 48  $\mu\text{m}$ , and the two LiTaO<sub>3</sub> pyroelectric transducers, cut out of the same wafer, had very similar electric and thermal properties. They had a thickness  $L_p = 280 \mu\text{m}$  and a very similar area  $A \cong 2 \text{ cm}^2$ .

Fig. 2 reports the results of  $\ln(A_T)$  and  $\Phi_T$  displayed as a function of  $(f)^{0.5}$  for the 8CB liquid crystal sample in the smectic phase at 30°C. As predicted by the model, they both behave linearly with  $(f)^{0.5}$  above a certain frequency, when the sample and the transducer become thermally thick. The continuous straight lines, representing the best fit of the linear behaviours, have very similar slopes  $m$  as predicted by the thermal terms in equations (5) and (6). It can be seen that the extrapolation of the linear behaviour of the phase crosses the zero value at zero frequency confirming that we are dealing with absolute values of  $\Phi_T = -L_s \sqrt{\frac{\pi f}{D_s}}$ . The value of  $m$  can yield the sample thermal diffusivity, and the offset at zero frequency of  $\ln(A_T) = -L_s \sqrt{\frac{\pi f}{D_s}} + \ln[2/(1 + \frac{e_p}{e_s})]$ , also the sample thermal effusivity. These ultimately lead to the determination of the specific heat  $c_s = e_s / \rho_s (D_s)^{0.5}$  and of the thermal conductivity  $k_s = e_s (D_s)^{0.5}$  of the sample. Note that the frequency scan is displayed just for convenience to prove the reliability of the adopted model but is not mandatory for the “absolute”

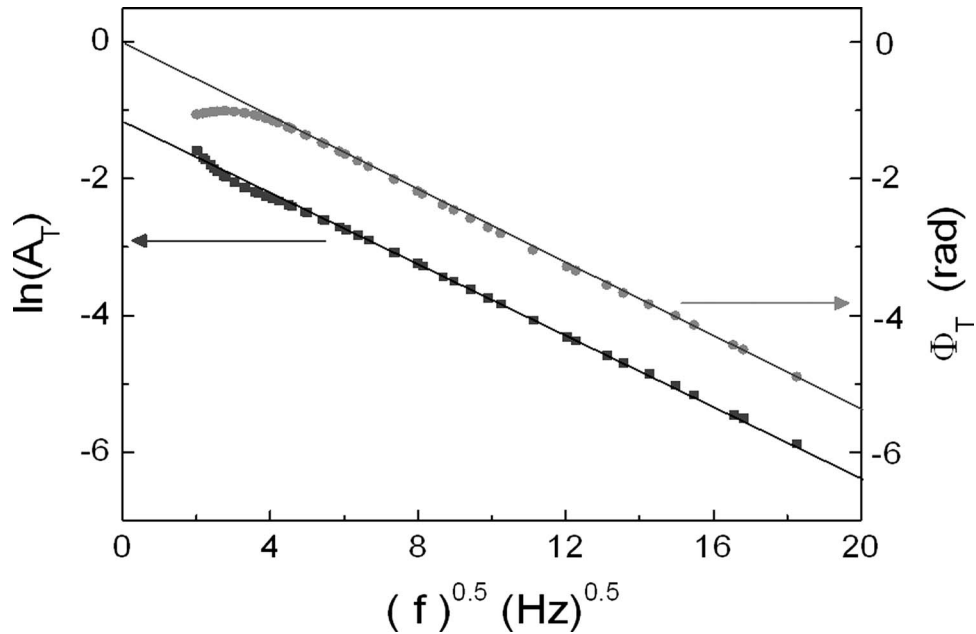


FIG. 2.  $\ln(A_T)$  and  $\Phi_T$  (see text) as a function of the square root of the frequency. Continuous lines represent best linear fit of high frequency data.

determination of the thermal parameters. The absolute values of  $\ln(A_T)$  and of  $\Phi_T$  obtained at a single frequency are, in fact, sufficient for such purpose.

The results in fig. 2 are very similar to the ones reported in ref. 17 where the RD signal for a sample was normalized to that obtained, separately, by illuminating a sample free pyroelectric transducer. In that work, where the authors investigated the degree of accuracy in the determination of  $D_s$  and  $e_s$  in various situations, the phase represents the absolute  $\Phi_T$  values. For the amplitude also to represent absolute values, care must be taken that the heating beam absorption conditions be the same for the signals obtained from the sample and from the transducer alone, and this involves an elaborate procedure.<sup>17</sup> With the method presented in this paper, the processed signal is independent of the intensity of any of the heating beams and none of such tedious procedures is necessary. The vs temperature measurements of the thermal parameters was performed at a frequency of 30 Hz, large enough to achieve the thermally thick regime and small enough to achieve an adequate signal to noise ratio. The results for the specific heat over the AN and NI phase transitions for the present measurements are displayed in fig. 3(a) together with those previously obtained by the “relative” PPE calorimetry,<sup>11</sup> results which, in turn, had already been shown to be in good agreement with all the other previously reported results obtained by the various calorimetric techniques.<sup>10-12</sup> The very good agreement between the two displayed data sets indicates the good reliability of the presently adopted configuration. Moreover, in fig. 3(a) it is shown that the temperature resolution is the same as that obtained previously where the critical exponents characterizing the critical behaviour of the specific heat could be determined over the smectic A - nematic phase transition.

Fig. 3(b) reports the thermal conductivity results obtained in the present work. In the nematic and in the smectic phases, the thermal transport properties strongly depend on the kind and degree of the average molecular orientation, which can be strongly influenced by the interaction with cell walls,<sup>11,19</sup> It turns out, in fact, that the thermal conductivity is larger when measured along the molecular axes than when perpendicular to it. Therefore, for a consistent comparison with the previous results, fig. 3(b) also reports the thermal conductivity temperature profiles for 8CB monodomain samples with molecules aligned perpendicular (homeotropic) and parallel (planar) to the cell walls, where the alignments were induced by the adequate treatment of the cell walls, obtained by means of the “relative” PPE calorimetry.<sup>11</sup> Here the results depend strongly on the reference value, chosen in the isotropic phase where it is independent of the cell wall conditions

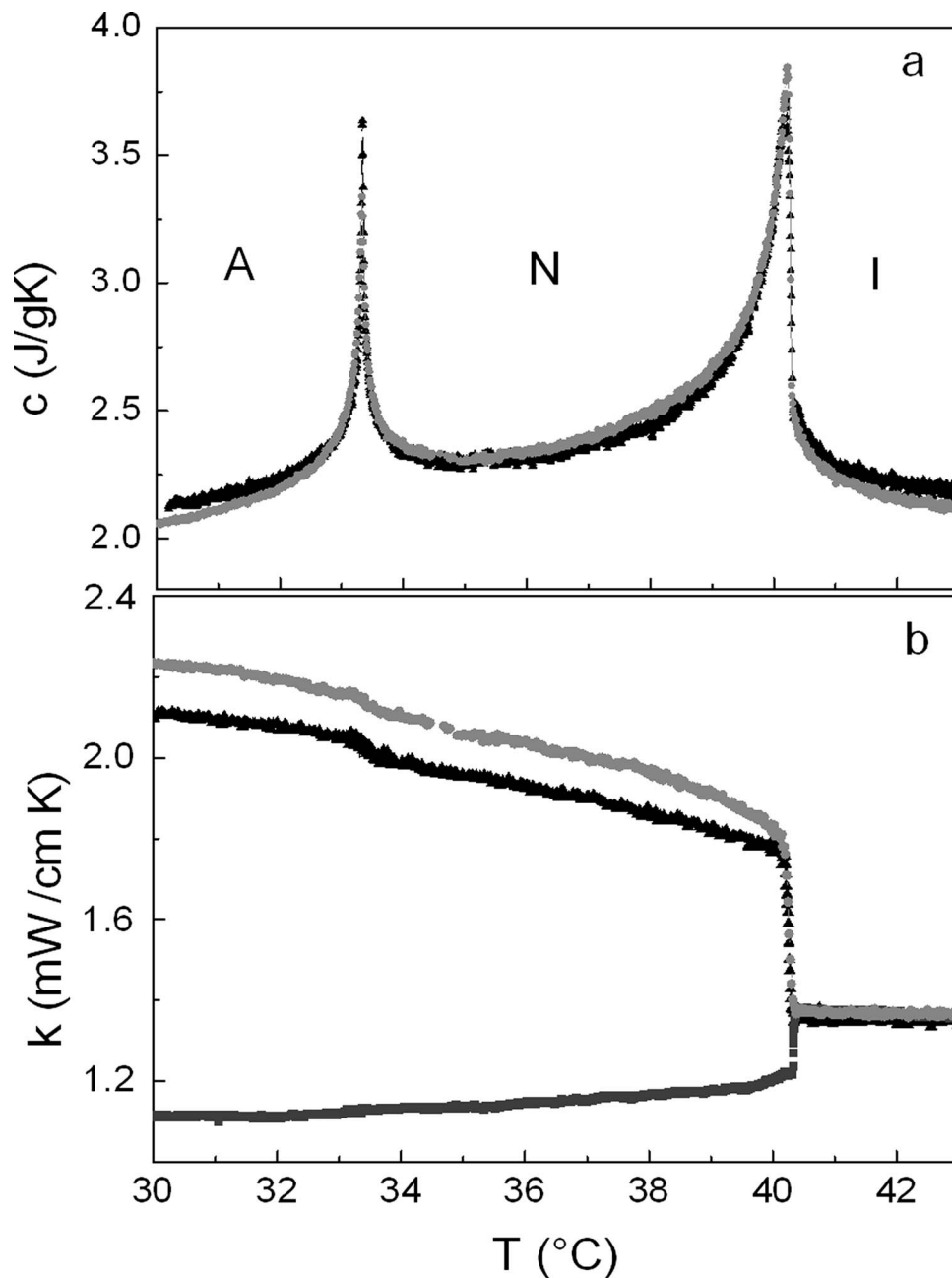


FIG. 3. Specific heat (a) and thermal conductivity (b) over AN and NI (see text) transitions in 8CB liquid crystal. Present work (black symbols), previous works (gray symbols) (see text).

because the sample molecules cannot align. With respect to the results reported in ref. 11, the results of  $k$  displayed in fig. 3(b) for the two aligned samples have been determined with different more reliable reference values in the isotropic phase, obtained from the rear detection signal phase frequency scan,<sup>1</sup> after a more accurate determination of the cell thickness and correction against the detection electronics intrinsic vs frequency response. It can be seen that, in the isotropic phase, even the values of  $k$  obtained with the “absolute” measurement carried out in this work, agree very well with the results obtained previously, once more indicating the soundness of the results obtained by the present method. In the smectic and nematic phases, where, as explained earlier on, larger values of  $k$  are expected and observed for the homeotropic alignment than for the planar one, the

values obtained with the present measurements are not far from those of the homeotropic sample, indicating that the cell wall conditions were such as to induce only partial homeotropic alignment of the sample molecules.

It must be remarked that, though the results presented in this work concern a liquid sample, the method can be applied to study phase transitions also in gels and in solids as previously performed by the “relative” PPE technique.<sup>18</sup> No application to gases has so far been attempted because of their substantial pressure increase with temperature inducing stray effects on the pyroelectric transducer which has also piezoelectric properties.

Previously, other methods had been used to obtain “absolute” measurements of the thermal parameters at a single temperature. To determine the thermal effusivity, the ratio of the sample signal amplitude in a PPE FD configuration to that of the bare pyroelectric transducer has been performed,<sup>20</sup> while the thermal diffusivity determination required the above mentioned frequency scan of the phase data.<sup>1</sup> A method where both  $c_s$  and  $k_s$  can be determined simultaneously is another where the FD PPE configuration<sup>12</sup> is adopted. It is rather complex and time consuming since, with a very thin layer of sample placed on a transducer, several frequency scans of the signal amplitude and phase need to be performed with a backing material placed at various known distances from the transducer itself.

The described methods are not easily applicable for vs temperature measurements, but they can be used to obtain the reference values for the thermal parameters required for the “relative” PPE calorimetry, as performed in ref. 12. Alternatively, such values may be obtained from the literature, when available. When thermal transport parameters of liquids are concerned, however, they must correspond to values in the isotropic phase, where no sample/cell wall interaction effects can take place. This may imply that, during the vs temperature measurement, the sample be taken to a temperature range which may be far off the one of interest. It must finally be born in mind that procedures involving frequency scans are not easily applicable to all kind of materials, such as those where glassy transitions are involved in which, as mentioned earlier on, the thermal parameters have an intrinsic frequency dependence. All these considerations point out to the importance of the present “absolute” PPE calorimeter which does not require reference values, and where no frequency scans are necessary.

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