

## **PHOTOPYROELECTRIC METHOD**

### **Determination of the thermal parameters of liquid crystals and antiferromagnetic materials close to the phase transitions**

*F. Mercuri, M. Marinelli, U. Zammit, S. Foglietta and F. Scudieri*

Dipartimento di Ingegneria Meccanica – II Università di Roma 'Tor Vergata',  
Via della Ricerca Scientifica e Tecnologica, 00133 Roma, Italy

#### **Abstract**

High resolution measurements have been performed with a photopyroelectric (PPE) technique to study the static and dynamic thermal parameters behaviour in the critical region of different liquid and solid samples. In particular the specific heat ( $c$ ), the thermal diffusivity ( $D$ ) and the thermal conductivity ( $k$ ) have been simultaneously determined in the critical region around the antiferromagnetic/paramagnetic (AP) phase transition occurring in  $\text{FeF}_2$  and around the Smectic-A/Nematic (AN) phase transition occurring in the 8S5 liquid crystal.

The high resolution of the measuring technique has allowed the determination of the  $c$  and  $D$  critical exponents and amplitude ratio of their critical terms.

**Keywords:** liquid crystals, phase transitions, photopyroelectric method

#### **Introduction**

Static and dynamic thermal parameters often show anomalous behaviours in the region around a transition temperature (critical region). The static critical phenomena associated with second order phase transitions can be described by different theoretical models (Ising, XY, Heisenberg) [1] depending on the system dimensionality and symmetry (number of components of the order parameter). Each model predicts particular values for the specific heat ( $c$ ) critical exponent and amplitude ratio of the critical term [2]. On the other hand, in order to describe the critical behaviour of the dynamic thermal parameters, i.e. the thermal diffusivity ( $D$ ) and the thermal conductivity ( $k$ ), analogous models have been developed predicting particular relations between static and dynamic critical exponents [3]. Therefore many of the conclusions in the study of the critical phenomena can be derived from the knowledge of the thermal parameters critical exponents and by a meaningful comparison between the static and the dynamic ones. To study the critical exponents of the thermal parameters, a technique which ensures their high resolution evaluation is required, while a technique which also enables their simultaneous measurements would ensure a

comparison of the critical exponents between static and dynamic quantities obtained in the same experimental conditions.

A large number of experimental data concerning the specific heat are available in the literature while very few high resolution measurements have been performed for the dynamic quantities due to the fact that transport properties ( $k$  and  $D$ ) measurement needs a thermal gradient in the sample which can crucially limit the resolution of the technique employed.

In this work we present a photopyroelectric technique (PPE) which has enabled us to perform simultaneous high resolution measurements of  $c$ ,  $D$  and  $k$  in different liquid and solid samples [4–6]. In particular, measurements have been performed in the critical region of second order phase transitions occurring in some antiferromagnetic materials and liquid crystal samples. The high resolution of the technique allowed the determination of the specific heat and thermal diffusivity critical exponents and the amplitude ratio of their critical terms providing fundamental information about the nature of each phase transition.

## Technique and theory

The photopyroelectric one is an a.c. technique that allows an adequate signal to noise ratio by introducing temperature oscillations at the sample surface smaller than 1 mK. This main feature makes the PPE technique very attractive to study the thermal parameters behaviour in the vicinity of a phase transition where these parameters strongly depend on temperature [7].

In Fig. 1 the most common configuration for a PPE measurement in the case of a solid sample is sketched.

A modulated incident light beam is absorbed at the sample surface generating temperature oscillations which propagate through the sample thickness and reach the opposite surface in thermal contact with the pyroelectric transducer.

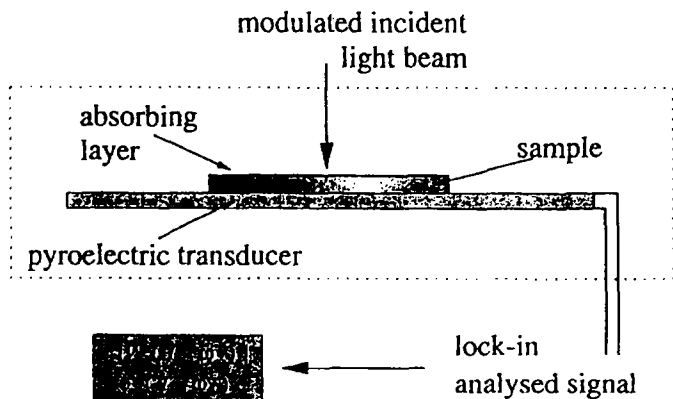


Fig. 1 Experimental set-up

The consequent temperature variation induced in the pyroelectric crystal generates an electrical signal, analysed by a lock-in amplifier, whose amplitude  $V$  and phase  $\varphi$  depend on the thermal properties of the sample. Under particular experimental conditions the theory predicts [8, 9] the following expressions:

$$|V| \propto \frac{1}{\sqrt{1 + (f/f_c)^2}} \frac{e_p e^{(-\sqrt{\pi f/D_s} L_s)}}{(e_s + e_g)(e_p/e_s + 1)} \quad (1)$$

$$\varphi \propto -\sqrt{\pi f/D_s} L_s \quad (2)$$

Here  $f$  is the modulation frequency,  $L_s$ ,  $D_s$ ,  $e_s = \sqrt{\rho_s c_s k_s}$ , and  $\rho_s$  are the thickness, the thermal diffusivity, the thermal effusivity and the density of the sample,  $f_c$  is the transducer plus detection cut-off frequency and  $e_p$  and  $e_g$  are the thermal effusivity of the pyroelectric and the front medium, respectively. From Eqs (1, 2) it can be noted how, once  $L_s$ ,  $f$ ,  $e_p$  and  $e_g$  are known, one can calculate  $D_s$  and  $e_s$ . Then, knowing also  $\rho_s$ , it is possible to determine  $c_s = e_s/\rho_s \sqrt{D_s}$  and  $k_s = e_s \sqrt{D_s}$ . Furthermore, at a fixed temperature, if  $f \gg f_c$ , the Eqs (1, 2) can be rewritten as  $\ln(f \times |V|) \propto -(\sqrt{\pi/D_s} L_s) \sqrt{f}$  and  $\varphi \propto -(\sqrt{\pi/D_s} L_s) \sqrt{f}$  respectively. It can be noted that in the conditions of validity of these two expressions (and therefore of Eqs (1, 2)) one should expect a linear dependence and with the same slope, of  $\ln(f \times |V|)$  and  $\varphi$  from the square root of frequency. Moreover, knowing  $L_s$ , an absolute evaluation of the thermal diffusivity can be obtained by measuring the angular coefficient. Figure 2 shows a frequency scan performed on a 620  $\mu\text{m}$  thick  $\text{FeF}_2$  sample at the temperature  $T=87.85$  K. From the slope of the solid straight line, representing the best data fit, the absolute thermal diffusivity value  $D=(0.196 \pm 0.016) \text{cm}^2 \text{s}^{-1}$  was obtained.

It is worth noticing that operating at low temperature does not represent a limit for the pyroelectric technique once transducer and sample are placed in thermal contact with a cryocooler cold finger. In fact we were able to use the PPE technique over a wide range of temperature (30÷400 K) for liquid as well as solid samples. The cell employed for liquid samples is sketched in Fig. 3.

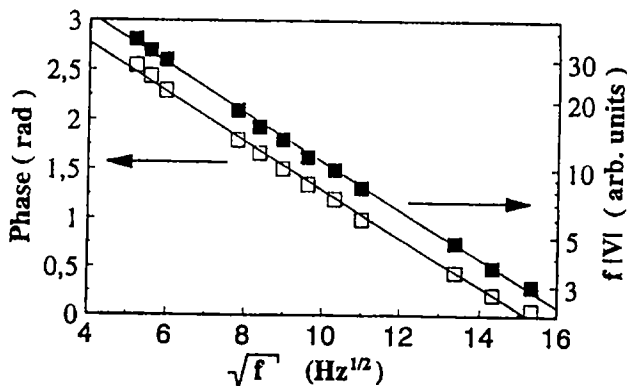


Fig. 2 Photopyroelectric phase and frequency-amplitude product vs. square root of frequency

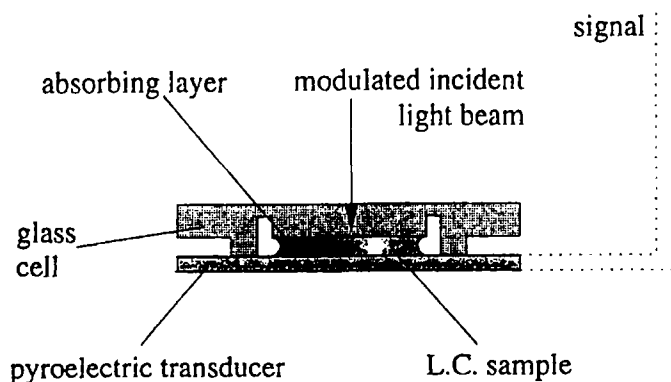


Fig. 3 Liquid samples cell

## Experimental results

The results reported in the present paper concern the thermal parameters critical behaviour of a  $\text{FeF}_2$  sample, showing its antiferromagnetic/paramagnetic (AP) phase transition at  $T_N = (78.55 \pm 0.02)\text{K}$  ( $T_N$ : Néel temperature), and of 8S5 liquid crystal sample which presents the Smectic-A/Nematic (AN) phase transition at  $T_{AN} = (336.200 \pm 0.004)$ .

In Fig. 4 the  $\text{FeF}_2$  data are plotted for  $c$  and  $D$  vs. reduced temperature  $t = (T - T_N)/T_N$ . The solid lines correspond to the best data fit obtained with the fitting functions

$$c = B + E(T - T_N) + A^\pm |T - T_N|^{-\alpha} \quad (3)$$

and

$$D = V + W(T - T_N) + U^\pm |T - T_N|^{-b} \quad (4)$$

where we consider  $|T - T_N|$  as  $|(T - T_N)/1\text{K}|$  and where  $\alpha$ ,  $A$ ,  $B$ ,  $E$  and  $b$ ,  $U$ ,  $V$ ,  $W$  are adjustable parameters, minus and plus superscripts corresponding to  $T < T_N$  and  $T > T_N$ , respectively. These functions consist of a linear part, representing the non-singular contribution, and a critical term responsible for singularities. From the specific heat best fit the values  $\alpha = 0.10 \pm 0.03$  and  $A^+/A^- = 0.53 \pm 0.08$  have been obtained, clearly confirming the Ising-like behaviour expected for uniaxial systems (dimensionality  $d=3$  and number of components of the order parameter  $n=1$ ). The Ising model predicts indeed a  $c$  critical exponent  $\alpha = 0.110 \pm 0.0045$  and an amplitude ratio of the critical term  $A^+/A^- = 0.51$  [10], which are in a very good agreement with our experimental values. Concerning the thermal diffusivity data, from the best fit we have obtained a critical exponent  $b = -0.11 \pm 0.04$ . In the case of uniaxial systems when the heat

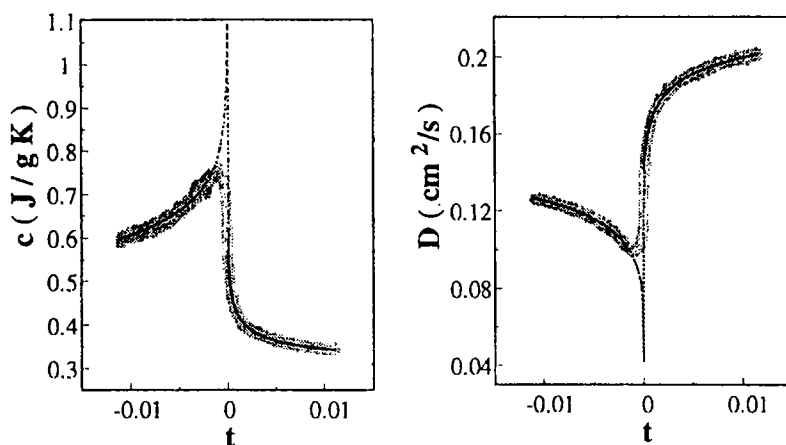


Fig. 4 FeF<sub>2</sub> specific heat and thermal diffusivity data vs. reduced temperature  $t = (T - T_N) / T_N$ . The solid lines represent the best fit from Eqs (3) and (4). The dotted lines represent the fit part corresponding to the rounding region where data are not considered

transport process is purely diffusive, the dynamic critical behaviour can be described in terms of a theoretical model (model C for  $n=1$ ) predicting  $-b=\alpha$  that is what we have obtained. The thermal conductivity behaviour (not shown) does not show any anomaly at  $T_N$  as one should expect being  $-b=\alpha$  within the experimental uncertainty.

In Fig. 5,  $c$  and  $D$  behaviour of the 8S5 are plotted over the AN phase transition region. Again data have been fitted with the same expressions used in the case of FeF<sub>2</sub>. For the specific heat the values  $\alpha = -0.022 \pm 0.008$  and  $A^-/A^+ = 0.968 \pm 0.020$  have been obtained. These experimental values are close to those ( $\alpha = -0.007$  and  $A^-/A^+ = 0.9714 \pm 0.0216$ ) predicted by the 3D XY model valid for systems with  $d=3$ ,  $n=2$  [11, 12]. The difference between the measured and the theoretical  $\alpha$  values can be explained through the dependence of the  $\alpha$  value on the width of the nematic range [13]. The thermal diffusivity critical exponent  $b = -0.027 \pm 0.005$  obtained from the fit is similar to the specific heat one and suggests the  $D$  critical behaviour to be described once again by the dynamic model C for  $n=2$  which predicts  $-b = |\alpha|$ . The thermal conductivity remains almost constant all over the critical region showing no anomaly at  $T_{AN}$ .

## Conclusions

The application of the PPE technique has enabled us to perform high resolution simultaneous measurements of thermal parameters in the vicinity of two second order phase transitions of solid and liquid samples. The investigated temperature ranges where the two transitions occur, are in the cryogenic temperature region and near the room temperature, respectively. For what concerns

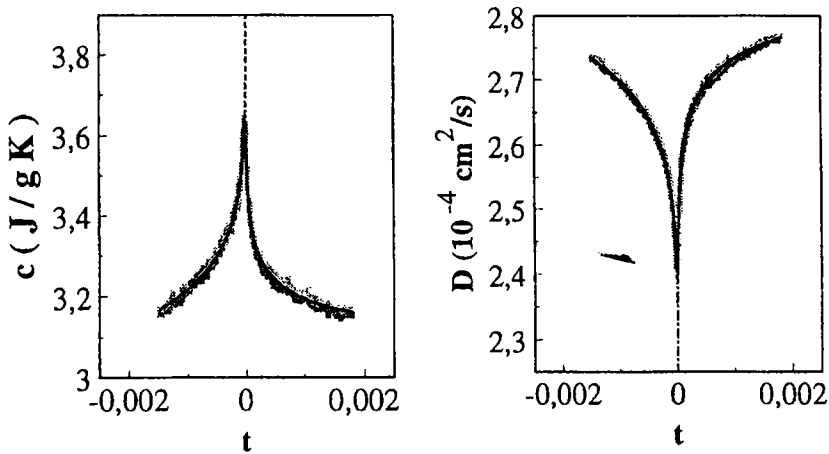


Fig. 5 8S5 specific heat and thermal diffusivity data vs. reduced temperature  $t=(T-T_{AN})/T_{AN}$ . The solid lines represent the best fit from Eqs (3) and (4). The dotted lines represent the fit part corresponding to the rounding region where data are not considered

the  $\text{FeF}_2$  its Ising like system nature has been confirmed and it has been shown how its thermal diffusivity critical behaviour can be described by the dynamic model C for uniaxial systems. Analogously it has been shown that for the 8S5 liquid crystal the 3D XY model in statics and the model C for  $n=2$  in dynamics well describe the  $c$  and  $D$  critical behaviour. For both of the samples the thermal conductivity presents no anomaly at the transition temperatures.

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