



A new application of the liquid thermoelectrics: The detection of magnetic phase transitions



D. Dadarlat, C. Tripon*

National R&D Institute for Isotopic and Molecular Technologies, Donat Str. 67-103, Cluj-Napoca, Romania

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ABSTRACT

During last years, both solid and liquid thermoelectric materials proved to be useful tools for thermal inspection of condensed matter samples. Used in contact techniques, the liquid thermoelectrics are very suitable in investigating the thermal properties of solids, mainly due to the perfect solid sample-liquid sensor thermal contact. The paper proposes a new application of the liquid thermoelectrics (LTE): the detection of phase transitions. In order to prove the suitability of this application, Cr₂O₃ single crystal was selected as a sample – Cr₂O₃ is a well-known antiferromagnetic material involved in a phase transition at a Néel temperature around 34 °C. A LTE material (octanol + 10⁻² mol/l tetrabutylammonium nitrate (TBAN)) was used as a sensor for the detection of the antiferro-paramagnetic phase transition of Cr₂O₃. Based on the recently developed theory of the photothermoelectric (PTE) method, the measured amplitude and phase of the complex PTE signal were converted in thermal parameters. As a consequence, the behavior of the static volume specific heat and dynamic thermal diffusivity, conductivity and effusivity of Cr₂O₃, around the Néel point, have been obtained. A comparison with similar investigations, obtained by using CuCrO₂ (a solid thermoelectric materials) as a sensor, was performed. The results obtained with LTE as a sensor proved to be more accurate, due to the previously mentioned “perfect liquid sensor-solid sample” thermal contact.

1. Introduction

In the critical region of a phase transition, a system passes from an ordered to a disordered phase. In the vicinity of the transition temperature, the order parameter (non-zero in the ordered phase) fluctuates and vanishes in the disordered phase. The critical fluctuations of the order parameter lead to critical anomalies for various quantities characterizing the system [1]. Consequently, if one intends to detect and study a phase transition, he must be able to measure a quantity (parameter) presenting an anomaly at the critical point. These parameters can be specific for different classes of materials (examples are: magnetization and/or magnetic susceptibility for magnets, polarization and/or electrical permittivity for ferroelectrics, etc.), but they can also characterize all types of materials. Among this last type of parameters we count the thermal parameters. Consequently, the methods (calorimetries) able to directly measure the thermal parameters are very suitable for phase transitions detection due to their degree of generality (a large range of materials can be investigated). Among these calorimetries, the contact photothermal techniques are of particular interest due to their sensitivity and to the fact that all static and dynamic thermal parameters can be obtained, sometimes from only one

measurement. For example, the photopyroelectric (PPE) method has been largely used in order to measure the thermal parameters and detect II-nd order phase transitions in various solids [2,3], ferroelectric and magnetic materials [4,5], superconductors [6], liquid crystals [7–9], as well as to study I-st order transitions such as meltings or glassy transitions [10–12]. On the other hand, recently, a new photothermal calorimetry, based on the so called photothermoelectric (PTE) effect, was proposed [13,14]. The method is rather similar with the PPE technique, but the pyroelectric sensor is replaced by a thermoelectric (TE) sensor. The physical mechanism in the case of the PTE technique relies to the Seebeck effect. It has been shown that this novel method allows for the determination of thermal parameters such as effusivity and diffusivity, both for the material used as sensor and/or to another material used as a sample, and several applications on liquids and solids have been already reported [13–17]. It has been also shown that solid TE materials can be suitable sensors for phase transitions investigations [18,19].

However, it is to be mentioned that, for contact PT techniques (as PPE and PTE) the quality of the sample-sensor thermal contact is responsible for correct and accurate results. Usual, the pyroelectric and thermoelectric sensors are solid materials and consequently, when

* Corresponding author.

E-mail address: carmen.tripon@itim-cj.ro (C. Tripon).

investigating solid samples, a coupling fluid is always necessary in order to perform a good thermal contact. Even if the thermal properties of the various coupling fluids used in experiments (silicone grease and oil, various mineral oils, ethylene glycol, water, even air, etc.) are known, due to the unknown thickness of the coupling fluid, the quantitative results are more or less influenced. A lot of work was dedicated during last years to control the thickness of the coupling fluid. One alternative was to use the so called thermal-wave resonator cavity (TWRC) method [20–25]. In this method, the chopping frequency of the incident radiation is kept constant, and a coupling fluid's thickness scan is performed. The advantage of the method consists in the fact that the data processing does not request the exact knowledge of the coupling fluid's thickness, but only its thickness variation, that can be accurately controlled. A second method used to minimize the influence of the coupling fluid on the values of the thermal parameters was to try to minimize the thickness of the coupling fluid by mechanical methods. Special cells have been designed for such a purpose [26]. A third alternative [27–30] was to take into account in the theoretical assumptions the coupling fluid as a non-negligible layer and to use its thickness as a fitting parameter. It was demonstrated that, in some particular detection cases, the thickness of the coupling fluid is independent on other fitting parameters (as thermal effusivity and diffusivity for example) and consequently, the fit performed with three or even four fitting parameters leads to unique solutions.

However, even if the methods presented before improved substantially the accuracy of the quantitative results when measuring the thermal parameters of solids, the best method is *not to use coupling fluid* between sensor and sample (if it is possible).

One alternative to avoid the insertion of the coupling fluid between a solid sample and a sensor is to make use of a liquid sensor. This is in fact the purpose of this paper. A liquid LTE material, octanol + 10^{-2} mol/l tetrabutylammonium nitrate was used as a sensor for a concrete thermal application: the detection of the antiferro-paramagnetic phase transition of Cr_2O_3 . Cr_2O_3 is a well-known antiferromagnetic material involved in a phase transition at a Néel temperature around 34°C [5]. A comparison with similar investigations, obtained by using the same material (Cr_2O_3) as a sample, and CuCrO_2 (a solid thermoelectric material) as a sensor, was also performed.

2. Theoretical aspects

The theory of the PTE detection of phase transitions was presented before [18,19]. We will give here only the final equations.

For a detection cell composed by two layers, (1) sample and (2) LTE sensor, in the back detection configuration (i.e. sample directly irradiated and sensor in back position), for opaque sample and thermally thick sample and sensor (meaning that the geometrical thickness of each layer is larger than the thermal diffusion length), the normalized PTE signal (normalization performed with empty sensor) is given by [18,19]:

$$\Delta V_n = \frac{2}{(b_{12} + 1)} \exp(-\sigma_1 l_1) \quad (1)$$

where standard notations have been used [18,19]

$$\sigma = (1 + \sqrt{-1}) \left(\frac{\omega}{2\alpha} \right)^{1/2}; \quad b_{12} = \frac{e_1}{e_2} \quad (2)$$

In Eqs. (1) and (2) α and e represent the thermal diffusivity and effusivity, respectively and $\omega = 2\pi f$ with f the chopping frequency of the incident radiation.

Starting from Eq. (1), a scan of the phase of the PTE signal as a function of temperature can provide the temperature behavior of the thermal diffusivity (including the phase transition region). The amplitude can be then used to obtain the temperature behavior of the thermal effusivity. For quantitative results, a calibration of the measurement, at a convenient temperature (T_0) must be performed. Using the values of

the thermal diffusivity α_0 and thermal effusivity e_0 at the normalization point we can derive, according to Eq. (1) the temperature dependent thermal diffusivity and effusivity across the critical temperature, as:

$$\alpha = \frac{\pi f}{\frac{\pi f}{\alpha_0} + \left(\frac{\Delta\theta}{l_1} \right)^2 - 2 \frac{\Delta\theta}{l_1} \left(\frac{\pi f}{\alpha_0} \right)^{1/2}}; \quad \Delta\theta = \theta - \theta_0 \quad (3)$$

$$e = \frac{V}{V_0} \exp(\Delta\theta) (e_0 + e_2) - e_2 \quad (4)$$

where V_0 and θ_0 represent the amplitude and the phase of the PTE signal at the normalization point.

3. Experimental

The experimental set-up used for PTE detection of phase transitions was described elsewhere [18,19,24,25]. We give here only some specific details. The radiation source was a 100 mW YAG laser, chopped from the internal generator of a SR 830 lock-in amplifier, used for data processing. The detection cell was provided with Peltier elements (coupled to a thermostatic bath) for temperature scans. The temperature variation rate was $0.5^\circ\text{C min}^{-1}$ and the temperature range, 28°C to 42°C , included the Néel temperature (34°C) for the antiferromagnetic-paramagnetic phase transition of Cr_2O_3 . Both data acquisition and data processing were computer controlled.

The investigated sample was a 10 mm in diameter and 0.515 mm thick Cr_2O_3 optically opaque single crystal [5]. The LTE sensor was produced by mixing and dissolving a salt of tetrabutylammonium nitrate -TBAN (Sigma Aldrich with a purity $\geq 99.0\%$) at concentration $c = 10^{-2}$ mol/l in octanol (purchased from Fisher Scientific, purity $\geq 98.0\%$) at ambient temperature. The mixtures were stirred and heated at around 40°C for 15 min, in order to improve salt solubility. The Seebeck coefficient of the resulting LTE was not measured, but it was supposed to be in the range $3\text{--}4 \text{ mV K}^{-1}$ [31,32].

A new cell, designed for the sensor-sample assembly, which allows a direct sample-sensor thermal contact, is presented in Fig. 1.

The LTE sensor accommodates the space inside a plastic cylinder, between a metallic electrode (Cu – 0.1 mm thick) and the sample. The thickness of LTE was 1 mm. At this thickness, both the amplitude and the phase of the PTE signal are saturated [17]. The rear side of the sample (Cr_2O_3) was deposited with a thin layer of silver and constitutes the second electrode for the PTE signal. The temperature scans have been performed at 3 Hz modulation frequency. At this modulation frequency, the requirement of thermally thick sample and sensor are fulfilled, as presented in Fig. 2.

In fact, if we calculate the critical frequency (the frequency for which the layer passes from thermally thin to thick regime) independently for LTE and Cr_2O_3 , we will find that, at 3 Hz, the LTE

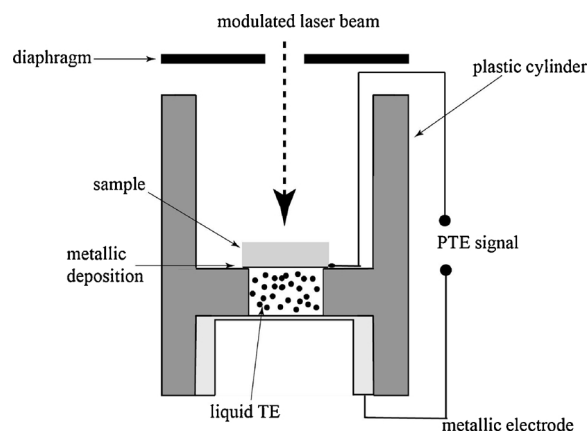


Fig. 1. Layout of the sensor-sample assembly used for PTE detection of phase transitions.

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