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SPECIFIC HEAT MEASUREMENTS UNDER NON-EQUILIBRIUM CONDITIONS

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Abstract

The application of conduction calorimetry for specific heat measurements on samples under non-equilibrium conditions is reviewed.

The influence of a constant rate of temperature decrease on the specific heat c of a TGS ferroelectric crystal doped with a small quantity of *L*-alanine (LATGS) is discussed. The relaxation process of c is likewise analysed.

The simultaneous measurement of c and the dissipative heat power $\dot{Q}$ in a LATGS crystal in an alternative electric field which produces hysteresis loops is also discussed. It is shown that this specific heat is the sum of the corresponding equilibrium values plus a term proportional to the derivative of $\dot{Q}$ with respect to temperature.

Keywords: conduction calorimetry, non-equilibrium conditions, specific heat

Introduction

During the past decade, conduction calorimetry (microcalorimetry [1]) has been successfully applied to perform simultaneous measurements of several thermal properties of solids in an applied electric field.

This method [2–4] allows the measurement of specific heats, thermal conductivities and pyroelectric coefficients, and deduction of the behaviour of other parameters, such as thermal diffusivity, electrocaloric coefficient, etc.

The most relevant points of conduction calorimetry were reviewed in a previous paper [5], where our results were compared with the findings of other authors.

The above results were obtained under equilibrium conditions, but this technique has recently been used to study the specific heat behaviour of a sample of triglycine sulphate (TGS) doped with alanine (LATGS) under non-equilibrium conditions, near its transition point. The influence of the heating rate on the specific heat has been studied [6] and its relaxation time has also been analysed.

The specific heat behaviour of a sample under dissipative conditions has similarly been studied. The specific heat and the dissipative heat power were

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measured simultaneously [7] and the experimental results were explained by solving the heat conduction equation for a solid with a dissipative term depending linearly on the temperature.

In the present paper, these results are reviewed, and the usefulness of this technique for the study of samples under non-equilibrium conditions is demonstrated.

Experimental

The sensor (Fig. 1) is made of two identical fluxmeters, each having $n=48$ cromel-constantan thermocouples connected in series. The thermocouple wires are 7 mm long and 0.25 mm in diameter. The inner junctions are attached to a silver plate, which serves as an electrode. A heater with a very small thermal capacity is attached to the silver plate and both are in thermal contact with the inner junctions.

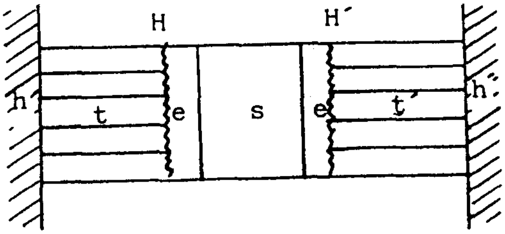

Fig. 1 Diagram of the thermopile: *t*, *t'*) thermocouples placed in series, *e*, *e'*) silver electrodes, *H*, *H'*) heaters, *h*) heat sink and *s*) sample

The two fluxmeters are placed with the silver plates facing each other, a plane parallel sample is pressed between them and constant stress is maintained on the sample. The (external) junctions on the other side are attached to a calorimeter block ensuring a very good thermal contact between them.

The block is supported within two cylindrical shields and the entire assembly is placed in a hermetic outer case where high vacuum can be produced. The temperature of the assembly and the measurements are controlled by a HP data acquisition system.

Because of the high vacuum in the calorimeter and since the temperature difference between the sample and the calorimeter block is lower than 0.1 K, lateral losses are negligible and linear heat conduction can be presumed.

The specific heat of the sample is measured by using the following procedure [2]:

We start from the steady state obtained when the same power W is dissipated in both heaters (H) in Fig. 1. This heat power W crosses through the fluxmeters, producing an emf V_0. At the initial time, the power is cut off and the emf V is integrated up to time t_1, when thermal equilibrium with the block is obtained and the emf reaches the constant value V_1.

We can consider three cases:

1. The measurements are carried out under equilibrium conditions with the temperature of the block kept constant. In this case, V_l is practically nil.
2. The measurements are carried out under quasistatic conditions, the temperature of the block being changed at a very low constant rate. In this case, V_l is very small because of the heat flux crossing the fluxmeter. This heat flux makes the temperature of the sample change at the same rate as the block temperature.
3. When there is a dissipative effect in the sample. In this case, V_l is proportional to the corresponding dissipative power.

It has been shown [2, 7] that in these cases the thermal capacity is obtained from

$$C = \frac{2n\varepsilon}{\alpha}(A - A_o) \qquad (1)$$

where

$$A = \int_0^{t_1} \frac{V - V_l}{V_o - V_l}\,dt \qquad \alpha = \frac{V_o - V_l}{W} \qquad (2)$$

ε and n are the thermoelectric power and the number of thermocouples, respectively, α is the sensitivity and A_o is the corresponding value of A when the experiment is carried out without sample (calibration of the calorimeter).

According to the above, this method allows:

1. study of the influence of very low heating rates on the specific heat;
2. study of the relaxing process when the temperature of the block is kept constant after change of the temperature of the sample;
3. the performance of simultaneous measurements of both the thermal capacity and the dissipative heat power of the sample under non-equilibrium conditions.

As examples of the above statements, in this paper we will discuss some specific heat measurements on crystals of TGS and of TGS doped with *L*-alanine (LATGS). Samples 0.8 cm^2 in cross-section and 0.3 cm high along the ferroelectric axis were studied. They were cut from two single-crystals grown [8] from an aqueous solution of TGS (in the case of the LATGS crystal, this solution contained 7 mol% of *L*-alanine/mol glycine+alanine). Electrodes were prepared on both faces by the evaporation and deposition of silver.

Experimental results

In Fig. 2 the specific heat of TGS is represented *vs.* temperature when the temperature is decreased at a constant rate ranging between 0.02 and 0.4 K h^{-1}.

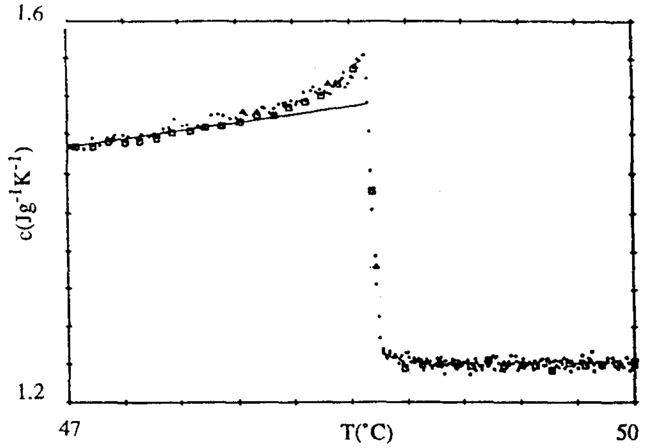

Fig. 2 Specific heat of TGS *vs.* temperature at different decreasing temperature rates: (•)–0.02 K h^{-1}, (□)–0.3 K h^{-1}, (▲)–0.4 K h^{-1}. Line: mean field theory prediction below T_0

Figure 3 compares data obtained by increasing and decreasing the temperature. From these Figures it can be deduced that the heating rate does not influence the obtained value of specific heat.

The specific heat jump and the transition width are greater and smaller, respectively on cooling than on heating. With regard to the effect [9] of an electric field on the TGS specific heat, this thermal hysteresis can be attributed to the fact that the small bias field acting in the crystal, due to the reticular defects, is lower on cooling than on heating. This thermal hysteresis appears only in the

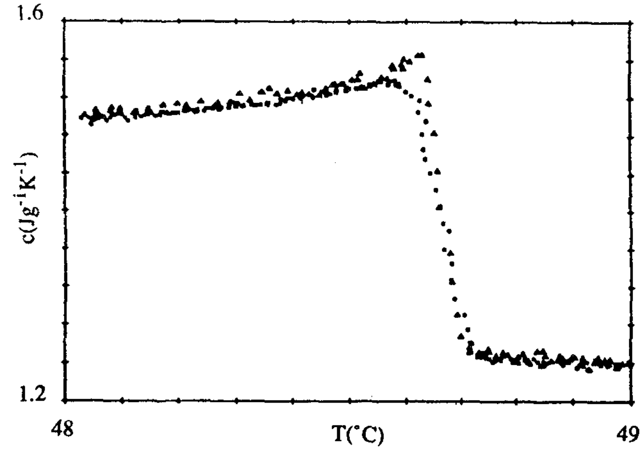

Fig. 3 Specific heat of TGS near the critical point: increasing (■) and decreasing (▲) temperature

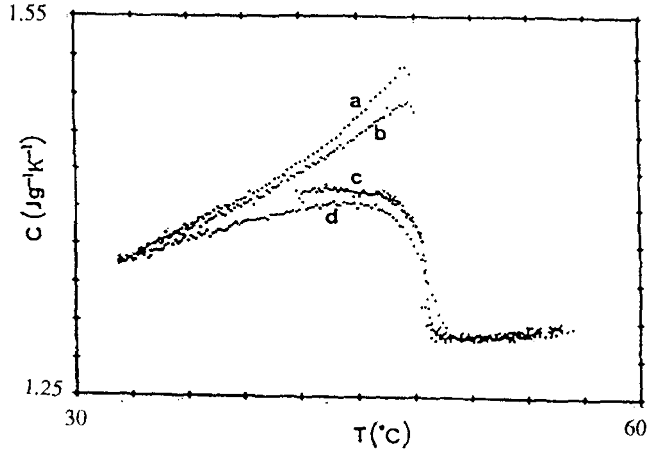

Fig. 4 Specific heat of LATGS *vs.* temperature at different temperature rates: a) -0.52 K h^{-1}, b) -0.24 K h^{-1}, c) -0.06 K h^{-1}, d) $+0.30$ K h^{-1}

temperature range where the data deviate from those for the classical mean field theory (continuous line in Fig. 2). This result agrees with that found previously by Strukov *et al.* [10].

The specific heat, c, of LATGS is represented *vs.* temperature in Fig. 4 for different cooling and heating rates of the sample, ranging from 0.06 to 0.52 K h^{-1}.

In the range of 15 K below the Curie point, the values of c obtained during heating are lower than those obtained during cooling. In this last case, the specific heat jump depends on the rate of temperature change. On the contrary the specific heat data obtained on heating do not depend on the heating rate. Fur-

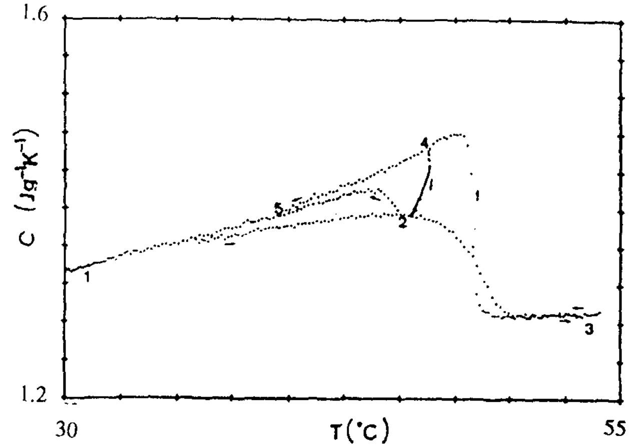

Fig. 5 Effect of thermal treatment on specific heat of LATGS

thermore, measurements carried out at a very low cooling rate (curve *c* in Fig. 4) tend to coincide with data obtained on heating (curve *d* in Fig. 4). Thus the heating data correspond to the equilibrium values.

This result is confirmed by the experiments depicted in Fig. 5 where, after heating (process 1 → 2 → 3), the sample is cooled (3 → 4), and at point 4 the temperature of the block is kept practically constant (process 4 → 2) for a long period (more than 35 h).

The specific heat relaxes to the equilibrium value (point 2 in the heating curve). This exponential relaxation is represented in Fig. 6, which allows deduction of a time constant of 14 h. This behaviour can be interpreted in the following way:

When TGS crystals are doped with molecules of alanine, only one sense of the polarization is stable. The molecules of alanine in the lattice of TGS cause an internal bias filed (B), which keeps the crystal permanently polarized [11]. This field B is a macroscopic parameter which includes all the microscopic factors that contribute to the partial or total unipolarity [12]. The monodomain state of the crystal is not only a result of the molecules of alanine, whose dipolar moment is unswitchable, but also due to the molecules of glycine that have been stabilized by the adjacent doped cells.

Thus it seems that B is produced by two factors: one (B_a) is due to the dipolar moment at the site of the alanines, and the other (B_g) is due to the displaced charges in the cells around the doped cells. When the alanine content is low, as in this sample, this second contribution is very significant. This second factor is thought to cause the above relaxation process.

As B decreases [12, 13] with the temperature, during cooling or heating B_g increases or decreases with time. It seems that the relaxation time of the decrease in B_g is very small with reference to the increase. Thus during heating,

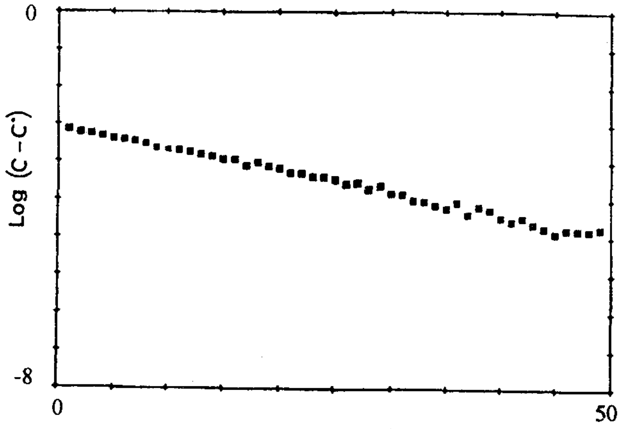

Fig. 6 Exponential relaxation of LATGS specific heat *vs.* time

the equilibrium value of B is obtained immediately. During cooling, the rate of acting bias field decreases with the rate of temperature change. Rates lower than 0.05 K h^{-1} are necessary to obtain the equilibrium value of B. On the other hand, similar behaviour has been found from pyroelectric measurements [14].

Finally, we present an example of specific heat measurements on a sample under dissipative conditions.

An alternative electric field of 1 kHz and several moderated amplitudes were applied to the LATGS crystal.

Since both the coercive field, E_c, and the bias filed, B, decrease with temperature, in the ferroelectric phase and near the transition point there is a temperature range which depends on the amplitude, where the crystal carries out minor or complete hysteresis loops. This produces a dissipation in the crystal. Below this range there is no dissipation because E_c+B is higher than the amplitude of the field; and above it, the crystal is in the paraelectric phase.

Due to the high frequency of the alternative field with reference to the thermal relaxation time of the crystal, we can assume a uniform internal dissipation, and therefore a steady temperature distribution in the crystal. This distribution depends on the dissipative power in the crystal.

According to the above, in the steady state obtained when there is no dissipation in the heaters H in Fig. 1, the dissipative heat power $\dot{Q}$ the crystal is evacuated through the fluxmeters and can be determined by measuring the emf V_1 given by them.

It has been shown [7] that in this case expression 1 allows determination of the steady thermal capacity, c, which is the relation between the heat exchanged by the crystal (without considering the heat due to the dissipative power) and the temperature variation on its boundary.

In Figs 7 and 8, the dissipative power and the steady thermal capacity are represented versus temperature for different amplitudes E_o ranging between 10 and 95 V cm^{-1}.

When there is no dissipation (E_o= 10 V cm^{-1}), c^* coincides with the equilibrium specific heat behaviour (E_o=0). In the range where there is dissipation, c^* shows a decrease or an increase at temperatures where the slope of $\dot{Q}$ is negative or positive, respectively.

This can be interpreted in the following way: during measurement (which implies a small increase in T) at a temperature where $\dot{Q}$ increases with T, the crystal passes from an initial state with a certain internal temperature distribution to another steady state whose temperature distribution is more pronounced because $\dot{Q}$ is higher. Thus, the enthalpy content, due to the internal temperature distribution, is higher, and it produces a greater effective steady thermal capacity. Obviously, the opposite effect is produced when $\dot{Q}$ decreases with T.

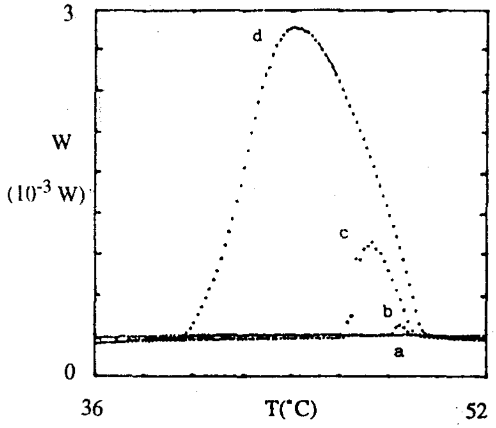

Fig. 7 Heat flux *vs.* temperature for different amplitudes E_0 of the applied alternative electric field: a) 10 V cm^{-1}, b) 27 V cm^{-1}, c) 61 V cm^{-1}, d) 95 V cm^{-1}

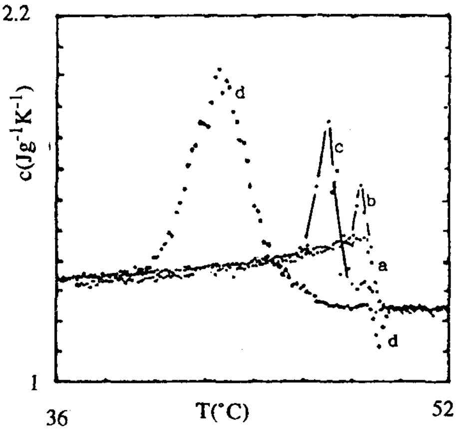

Fig. 8 LATGS specific heat *vs.* temperature for different amplitudes E_0 of the applied alternative electric field: a) 10 V cm^{-1}, b) 27 V cm^{-1}, c) 61 V cm^{-1}, d) 95 V cm^{-1}

To deduce the relation between c^* and $\dot{Q}$, the heat conduction equation of a solid bounded by two parallel planes with a uniform internal heat production σ, which depends linearly on temperature ($\sigma=\sigma_0+\eta T$), has been studied [7].

In has been found [7] that the above steady thermal capacity, c^*, can be expressed as

$$c^* = c + \frac{1}{2\eta}\frac{\partial\dot{Q}}{\partial T}\left(\left(\frac{L^2\eta}{h}\right)^{1/2} \coth\left(\left(\frac{L^2\eta}{h}\right)^{1/2}\right)-1\right) \qquad (3)$$

where L and h are the width and thermal diffusivity, respectively, of the sample.

From the thermal properties of the LATGS sample [15] and the data in Fig. 7, it is estimated that

$$\left(\frac{L^2\eta}{h}\right) < 8\cdot10^{-2} \tag{4}$$

Accordingly considering the coth series in expression (3):

$$c^* \approx c + \frac{L^2\partial\dot{Q}}{6h\partial T} + \ldots \tag{5}$$

This expression indicates that c^* is equal to the equilibrium value c plus a term corresponding to the variation in the enthalpy content in the sample, which is proportional to the derivative of the dissipative power with respect to temperature.

This statement is supported by Fig. 9, where a term proportional to the derivative of the data of $\dot{Q}$ represented in Fig. 7 corresponding to $E_o=95$ V cm^{-1} (curve *d*) has been added to the equilibrium behaviour represented by curve *a* in Fig. 8. Behaviour very similar to that of curve *d* in Fig. 8 ($E_o=95$ V cm^{-1}) was obtained.

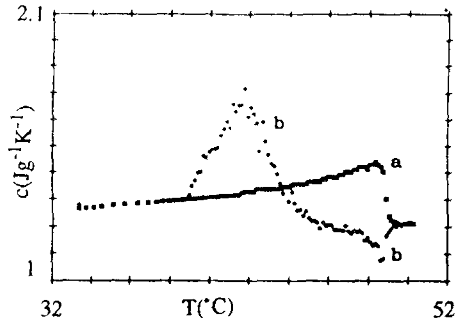

Fig. 9 a) LATGS specific heat *vs.* temperature at nil electric field. b) Data of curve (a) plus a term proportional to the derivative of curve (d) in Fig. 7

Conclusions

A previous paper demonstrated the usefulness of conduction calorimetry for simultaneous measurements of the thermal properties of a solid in an applied electric field. Relative to other techniques, it is possible to apply higher fields because the dissipated heat, due to the Joule effect, is evacuated from the crystal through the fluxmeter. Another advantage is that it is possible to measure several properties on the same sample and under similar conditions (specific heat, thermal conductivity, polyelectric coefficient, etc.) and to deduce the behaviour of others.

The possibility of carrying out measurements at constant temperature or at a very low constant rate of temperature change, allows the study of relaxation problems and the clear establishment of the influence of this rate on other specific heat behaviour.

These results reveal that it is necessary to pay attention to specific heat measurements in the ferroelectric literature, mainly when differential scanning calorimetry has been used.

On the other hand, the possibility of simultaneously measuring the heat power crossing the fluxmeter and the thermal capacity of the sample makes this technique very appropriate for the study of samples under dissipative conditions.

We consider that this method would be very appropriate for the study of the thermal capacity behaviour very close to a first-order transition. When the sample temperature is changed at low constant rate, the evolution of the emf V_1 would allow determination of the heat power $\dot{Q}$, due to the phase transition, and from integration of this to calculate the latent heat. However, in our opinion, the most important point is that the specific heat at the first-order transition point is very high [16] because the measurement is affected by the transition heat. The simultaneous measurement of c and $\dot{Q}$ allow a discrimination of this effect. Such a study is now in progress.

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