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2006 J. Phys.: Condens. Matter 18 10075

(http://iopscience.iop.org/0953-8984/18/44/007)

INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **18** (2006) 10075–10083 doi:10.1088/0953-8984/18/44/007

Influence of a weak dc electric field on tricritical phase transition in TGSe: evidence of different specific heat behaviour on cooling and heating runs

F J Romero, M C Gallardo, J Jiménez and J del Cerro

Departamento de Física de la Materia Condensada, Instituto Ciencia Materiales Sevilla, Universidad de Sevilla-CSIC, PO Box 1065, 41080 Sevilla, Spain

E-mail: fjromero@us.es

Received 7 April 2006, in final form 22 September 2006
Published 20 October 2006
Online at stacks.iop.org/JPhysCM/18/10075

Abstract

The para-ferroelectric tricritical phase transition of a single crystal of triglycine selenate (TGSe) has been studied in the neighbourhood of the transition temperature, under weak electric fields, E, using a highly sensitive calorimetric technique. The specific heat, c_E, under fields in the range between 5 and 175 V cm^{-1} and close to transition temperature (0.2 K), shows different behaviour on cooling and on heating at a temperature variation rate of ± 0.03 K h^{-1}; for $T < T_c - 0.5$ K all sets of data match each other. The experimental data have been fitted to the 2–6 Landau potential obtained for $E = 0$; a term $-\xi Q$, taking into account the coupling between E (ξ being dependent on E) and the order parameter Q, is included. This potential fits well with the experimental data in the ferroelectric phase. The different relation between ξ and E obtained on heating and on cooling runs is discussed and it is concluded that data on heating correspond to the thermal equilibrium.

1. Introduction

Triglycine selenate [$(NH_2CH_2COOH)_3H_2SeO_4$], hereafter TGSe, is a well-known uniaxial ferroelectric substance belonging to the triglycine sulphate (TGS) family, which undergoes a typical order–disorder phase transition at about $T \sim 22\,^{\circ}$C, the space group of the lower-temperature phase being $P2_1$ and that of the higher-temperature phase $P2_1/m$ [1, 2].

In a previous paper [3], we analysed the phase transition in a high-purity sample of TGSe by calorimetric measurements. No latent heat was detected, showing that the phase transition is continuous. No difference was found between specific heat data on cooling runs and on heating runs. The specific heat of the ferroelectric phase was found to follow a classical tricritical Landau potential, $\Delta G = \frac{1}{2}A(T - T_C)Q^2 + \frac{1}{6}CQ^6$, where Q is the normalized order parameter, $Q = P/P_0$, P is the spontaneous polarization and P_0 is the spontaneous polarization at

$T = 0$ K and the values of the coefficients were evaluated to be $A = 0.0814$ J g^{-1} K^{-1}, $C = 24.05$ J g^{-1} and $T_c = 295.49$ K.

In that work [3] we also showed that the specific heat anomaly of TGSe decreases under a weak uniaxial stress of 10 bar and, in the temperature range $|T_c - T| < 0.2$ K, data of specific heat on cooling runs does not match those of heating runs. While the data on cooling experiments showed a sharp anomaly, the data on heating runs were slightly smeared around the transition point. In contrast, cooling and heating data did match each other for stress-free experiments. This fact was related to the great influence of the stress on the relaxation time of domain growth, in such a way that, even for low temperature variation rates ($\mathrm{d}T/\mathrm{d}t = 0.03$ K h^{-1}), specific heat values on cooling runs are not equilibrium values, unlike those obtained on heating runs.

On the other hand, the influence of electric field on the dielectric susceptibility of TGSe was measured by Fugiel and Mierzwa [4]. They fitted the equation of state corresponding to a tricritical Landau potential under electric field, E, and reported values of A, C and T_c. Nevertheless, data close to the transition temperature ($T_c - 0.6$ K $< T < T_c$) were excluded from the analysis because of their deviations from the tricritical Landau scaling function.

Recently, we also studied the influence of a dc electric field in the phase transition of TGSe [5]. The specific heat was measured under several electric fields in the range 175–750 V cm^{-1}. We found that specific heat data for cooling and heating runs for a given field matched each other.

The theoretical specific heat derived from the Landau theory analysis by Fugiel and Mierzwa [4] matched experimental data in the paraelectric phase, but disagreements arose as the transition temperature was approached. We should stress that it is in this neighbourhood where the influence of the electric field on the specific heat becomes significant. This neighbourhood was also outside the study in the aforementioned work. In this region different contributions, such as domain arrangements, surface layer effects, local electric fields or even the sharp variation of polarization with temperature, may cause the 'effective field' in the sample to be different from the applied electric field. These effects are sometimes even present in the paraelectric phase.

In order to explain the data around the specific heat maximum, specific heat data was fitted to a 2–6 Landau potential with a coupling term $-\xi Q$, where $\xi(E)$ was an adjustable parameter in the fitting procedure [5]. We assumed that A, C and T_c were field independent, so their values were fixed to those obtained for $E = 0$ [3].

From this analysis, we obtained that, close to the transition temperature, the field ξ conjugated to the order parameter was not proportional to the external field but showed a general linear dependence, that is, $\xi \propto (E + E_0)$, where E_0 was evaluated to be about 150 V cm^{-1}.

Following this idea, and taking also into account the influence of weak uniaxial stresses on TGSe, the study of weak fields, i.e. fields lower than E_0, is doubtless of interest to ascertain the behaviour of the effective field. This is the goal of this paper, in which we complete the study of the influence of electric field on specific heat by carrying out experiments in the range 5–125 V cm^{-1}. Specific heat data, for both cooling and heating runs, will be analysed within the framework of the classical Landau theory in the same way as was done previously for stronger fields.

2. Experimental details

The TGSe sample is the same that was used in previous experiments [3, 5] and was prepared at the Institute of Physics, Adam Mickiewicz University, Poznan, Poland. It was parallelepiped with a thickness of 2.72 mm and an area of 55 mm^2. The main faces were prepared perpendicular to the b-axis and gold electrodes were evaporated onto them.

Measurements of the specific heat were performed in a high-resolution conduction calorimeter, which has been described in detail in [6].

The specific heat of the sample under an applied electric field has been measured using the method previously described in [7, 8].

3. Results and discussion

The specific heat c_E was measured on cooling and heating runs and under several electric fields ($E = 5, 15, 25, 75$ and 125 V cm^{-1}). The electric fields were applied in the paraelectric phase, 10 °C above the transition temperature, and remained constant during the cooling and heating process. The experiments were carried out under quasi-static conditions at a temperature scanning rate of 0.03 K h^{-1} to determine precisely the specific heat anomaly (a value of specific heat is obtained every 0.006 K).

For the analysis of the data, we assume that the baseline of the specific heat, needed for excess specific heat determination, was that of $E = 0$ run [3].

Figure 1 shows the specific heat excess, Δc_E, versus temperature for each electric field. To make the comparison between the different experiments easy, in each graph the prediction of the 2–6 Landau potential fitted for $E = 0$, obtained previously [3], is also represented. For clarity, the specific heat excess data for $E = 0$ are shown only in the graph for $E = 125$ V cm^{-1}, showing very good agreement between the data and the Landau prediction [3].

For heating and cooling runs, the influence of the electric field is to decrease the anomaly and to broaden it to higher temperatures, making the tail more significant at higher temperatures. These results are in agreement with those previously reported for higher electric fields [5, 9].

Nevertheless, in the ferroelectric phase and close to the transition temperature ($T > T_c - 0.2$ K), the influence of the applied electric field on heating is more significant than on cooling. At the transition temperature, specific heat data on the cooling run are higher than on the heating run for a given field. This fact is more significant for lower electric fields. While on cooling, for 5 V cm^{-1}, the curve is very similar to the data for $E = 0$ V cm^{-1}, on heating the anomaly decreases as if a stronger electric field were acting (figure 1). This may be equivalent to considering an 'effective field' which is higher on heating than on cooling. These results were not previously obtained for higher electric fields, where data on cooling and heating runs matched each other over the whole temperature range, as in the experiment for $E = 0$. Nevertheless, different behaviour of heating and cooling runs was previously obtained for specific heat data for $E = 0$, but under a weak uniaxial stress [3]. Similar results were also obtained by Jiménez *et al* for the specific heat of TGS doped with L-alanina (LATGS) [10].

In figure 2, maximum values of specific heat excess versus the applied electric field are shown. Data for higher electric fields, reported in a previous paper [5], are also shown. We observe that the difference between cooling and heating data decreases as the electric field increases. This fact is also shown in the inset, where the difference between specific heat maxima for cooling and heating runs for each field is represented. This difference disappears for $E = 175$ V cm^{-1}.

We now study the applicability of classical tricritical Landau theory to describe the specific heat data under an electric field. Fugiel and Mierzwa [4] assumed that the influence of the electric field enters through $-EP$ in the power expansion, where E is the applied electric field and P is the spontaneous polarization (the order parameter). The experimental specific heat data for $E = 250$ and 500 V cm^{-1}, and the theoretical specific heat from the Landau potential

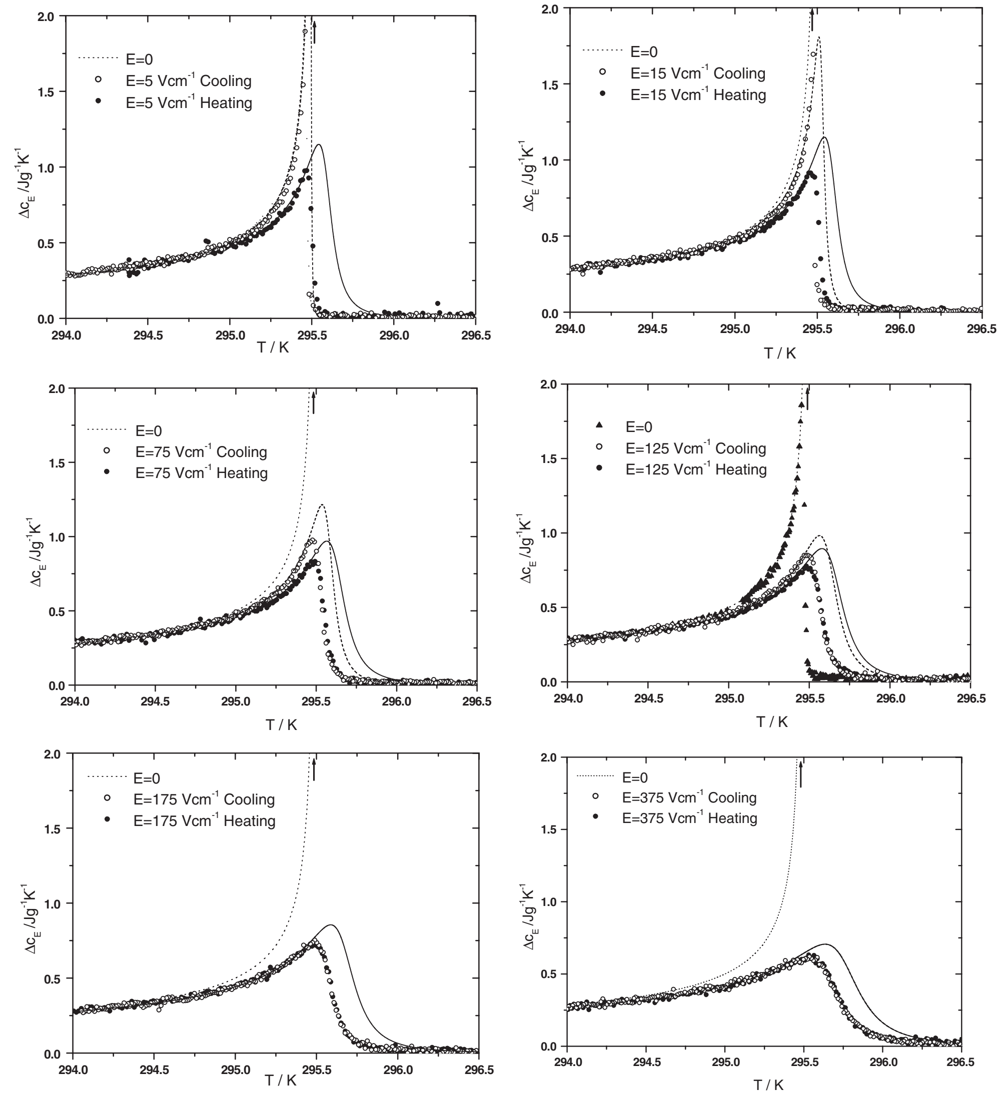

Figure 1. Specific heat excess of TGSe versus temperature on cooling and heating runs at $dT/dt = 0.03$ K h^{-1} for different applied electric fields. In each graph the predictions of the 2–6 Landau potential for $E = 0$ are also shown (dotted line). Specific heat data for $E = 0$ are shown in the plot for $E = 125$ V cm^{-1}. The best fit of a 2–6 Landau potential plus the term $-\xi Q$ is also shown for cooling runs (dashed) and heating runs (solid).

determined by Fugiel and Mierzwa [4], are shown in figure 3. At temperatures $|T - T_c| > 0.5$ K, a specific heat anomaly follows the prediction; in contrast, around the transition point the prediction fails, the experimental values being lower than the Landau prediction. It is noticeable that in the ferroelectric phase the prediction for $E = 500$ V cm^{-1} matches the experimental data for $E = 250$ V cm^{-1}, as if a higher field were acting on the sample in the ferroelectric phase.

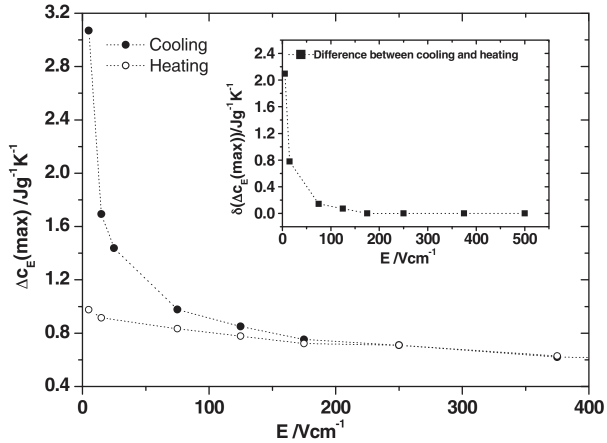

Figure 2. Maximum values of specific heat excess versus external electric field for cooling (filled circles) and heating (open circles) runs. The inset graph shows the difference in the maxima between heating and cooling runs versus electric field. The points have been linked by a line as a guide to the eye.

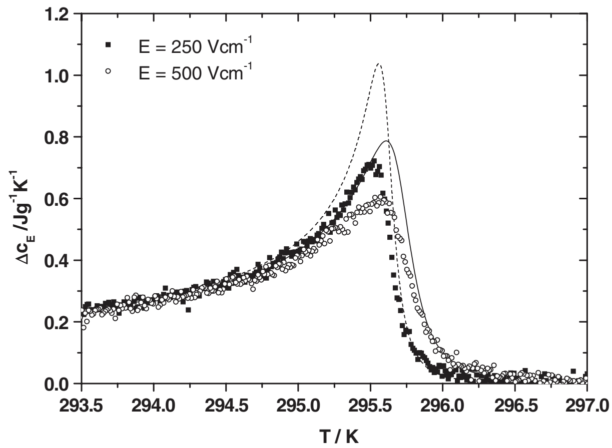

Figure 3. Experimental specific excess heat data for $E = 250$ V cm^{-1} (filled squares) and 500 V cm^{-1} (open circles), and the theoretical specific heat excess obtained from the equation of state of Fugiel and Mierzwa [4] for $E = 250$ V cm^{-1} (dashed line) and 500 V cm^{-1} (solid line).

These facts suggest that we assume that the influence of the electric field would be better included by means of a term $-\xi Q$ in the power expansion, so that:

$$\Delta G = \tfrac{1}{2}A(T - T_c)Q^2 + \tfrac{1}{6}CQ^6 - \xi Q \tag{1}$$

where $\xi(E)$. Note that, as Q is dimensionless, the dimension of ξ is that of energy. We assume that the values of the coefficients A, C and T_c are those of the $E = 0$ experiment which were determined previously [3] and quoted in section 1. Hence ξ will be the adjustable parameter in the analysis. This procedure was explained in a previous work for higher electric fields [5].

Following this idea, the value of ξ that best fits specific heat data at each temperature is determined, in such a way that ξ_i is obtained for each experimental point. The fitting routine

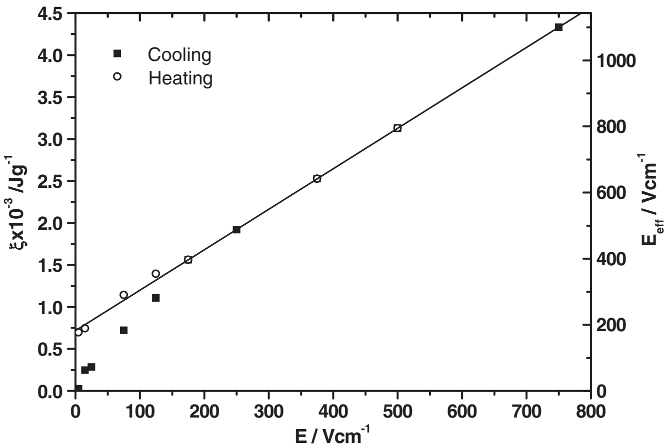

Figure 4. Fitted parameter ξ versus the applied electric field E, obtained for each specific heat curve on cooling (filled squares) and on heating (open circles). The right axis shows the corresponding values of $E_{\rm eff}$ (a rescaling of ξ).

will give us the value ξ that best explains the experimental specific heat data in the frame of this model, which uses an expression of free energy analogous to the Landau description.

If this model is suitable for explaining the experimental data, the whole temperature dependence of specific heat should be described with the same fitting parameter and, then, ξ_i should be temperature independent, within statistical uncertainty. In other cases, the temperature interval where ξ_i changes shows the region where this model is not fulfilled.

For each electric field, the specific heat data for $T < T_{\rm c}$ (ferroelectric phase) was successfully fitted with an average parameter ξ, whose values for the data obtained on cooling runs and on heating runs versus applied electric field are shown in figure 4.

Using those values of ξ in equation (1) along with the values of A, $T_{\rm c}$ and C for $E = 0$ [3], we have computed the theoretical Δc_E, which are shown in each graph of figure 1 by a solid line for heating runs and by a dash line for cooling runs. Experimental data and theoretical expectations agree in the ferroelectric phase for every field, on both heating and cooling runs.

In contrast, the values of ξ fitted in the paraelectric phase are temperature dependent, which means that the proposed Landau model does not describe the behaviour of the experimental Δc_E in that phase. Hence it is not possible to find a fitting field that simultaneously describes data for both the ferroelectric and the paraelectric phases. In figure 1, the theoretical predictions obtained for the ferroelectric phase are shown also in the paraelectric phase. The predictions do not follow the experimental values for the specific heat (the latest falling lower) but it is noteworthy that the shapes of the experimental data and the expectations are quite similar.

Figure 4 shows the parameter ξ which best fits the specific heat data for $T < T_{\rm c}$ versus the applied electric field. The values of ξ obtained on heating runs show a linear dependence on the electric field which does not cross the abscissa at the origin. This dependence is the same as that obtained for higher electric fields previously [5], also shown in figure 4. This result suggests that the field ξ in equation (1) is related to the external electric field, E, as $\xi \propto (E + E_0)$, where $E_0 \sim 150$ V cm^{-1}. Then, in order to fulfil the model, the field ξ conjugated to the order parameter will not be simply the external field. In other words, if the experimental data were explained within a model that uses an expression of free energy in the frame of the Landau description, as Fugiel and Mierzwa [4] did, an electric field higher than the applied electric field in the term $-EP$ of the power expansion would be needed. We will refer to this electric

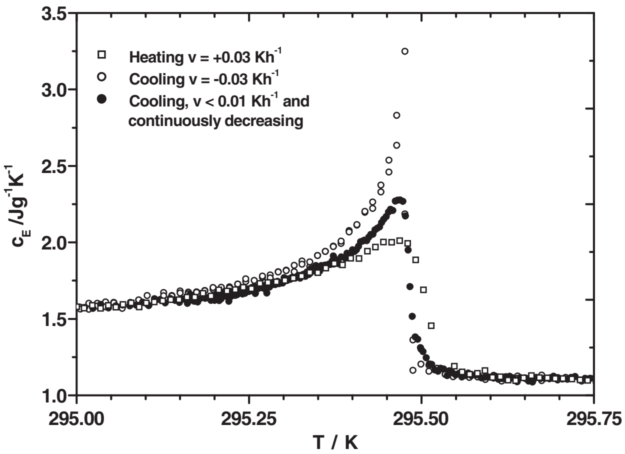

Figure 5. Specific heat excess versus temperature for $E = 15$ V cm^{-1} for heating (open squares) and cooling (open circles) runs at constant rate ($\mathrm{d}T/\mathrm{d}t = 0.03$ K h^{-1}) and for cooling runs in which $\mathrm{d}T/\mathrm{d}t$ decreases monotonously to zero (solid circles).

field as the effective field E_{eff}, and it is related to ξ by an appropriate scaling parameter. The right-hand axis of figure 4 shows the corresponding values of the effective field E_{eff}.

Figure 4 also shows the parameter ξ, obtained for cooling runs, versus the applied electric field, E. When the applied field is higher than E_0, the effective field is the same when heating from the ferroelectric phase as when cooling from the paralectric phase. Nevertheless, we observe that the values of ξ on cooling for $E < E_0$ clearly deviate from the linear tendency obtained on heating and on cooling runs for $E \geqslant E_0$, showing an inverse plateau.

The fact that the specific heat data on cooling runs are higher than those obtained on heating runs was previously reported in triglycine sulphate doped with L-alanine (LATGS) [10], but in that case the different behaviour spreads over a temperature interval of 15 K. In one experiment the specific heat of LATGS was measured under cooling conditions at a constant temperature scanning rate. Then, when the sample was in the ferroelectric phase, the cooling process was stopped and so the temperature was fixed. The specific heat data then showed an isothermal relaxation to those corresponding to the heating experiment. This relaxation was characterized by an exponential decay whose time constant was found to be 14 h. This result showed that the specific heat data on heating runs were close to the equilibrium values, while the specific heat on cooling runs depended on the temperature variation rate.

This result suggests performing a similar experiment in TGSe. However, it was not possible to carry out such an experiment, because of the large thermal inertia of the equipment and the small temperature interval (0.2 K) where the data on cooling and heating disagree. As an alternative experiment, the specific heat of TGSe for $E = 15$ V cm^{-1} was measured on cooling at a continuously decreasing temperature variation rate (from 0.01 K h^{-1} near the transition temperature to 0 K h^{-1} at 0.25 K below the specific heat maximum). Figure 5 shows the specific heat data from this experiment, together with the data obtained on heating and cooling the sample at a constant rate (0.03 K h^{-1}) and under the same applied electric field versus temperature. Our technique provides enough experimental data in that region and has enough resolution to show the difference clearly. This effect could be masked by other techniques that have worse temperature resolution.

It is observed that the data in the experiment where the temperature scanning rate is decreased continuously are closer to those for the heating run than those corresponding for a cooling run at 0.03 K h^{-1}. They move toward the heating data as the temperature variation rate decreases. This fact suggests, in analogy with the LATGS case, that the specific heat data of TGSe on cooling runs do not represent equilibrium values.

To confirm this result, we have applied the previously described fitting routine to the data obtained in this cooling run, and the value of ξ at each temperature was found. For this experiment, ξ is not constant and exhibits intermediate values between the corresponding values for the heating and cooling runs at a constant rate. As the temperature variation rate decreases, the values of ξ go to those obtained for the heating run, in agreement with the idea exposed above.

These results confirm that the data obtained on heating correspond to thermal equilibrium, and it would be necessary to measure the specific heat at an extremely low cooling temperature scanning rate to obtain equilibrium data.

4. Conclusions

We have studied the influence of a very low applied electric field on the specific heat. Different behaviour on heating and on cooling has been found, with some remarkable results.

We have shown that the behaviour of Δc_E in the ferroelectric phase and close to T_c is described by a Landau-like potential where an 'effective field' higher than the applied electric field is needed. This effective field is not actually a bias field, because its influence does not change if the field is reversed. It may be a consequence of the interaction between the external field and different effects such as surface layer effects, local electrics fields, due to, for example, the significant variation of spontaneous polarization with the temperature, or domain growth kinetics.

The value of this effective field is different for cooling runs than for heating runs at each applied electric field. On heating runs, when the ferroelectric phase is well established, the effective field is constant and the temperature variation rate is independent. The relation between the effective and applied electric fields is found to be that obtained previously for applied fields higher than $\sim$170 V cm^{-1}.

It is noteworthy that the specific heat for a short-circuited sample is very well represented by a Landau tricritical potential, on both cooling and heating runs, and they matche each other. In sharp contrast, the application of a field as low as $E = 1$ V cm^{-1} causes a strong change in the specific heat data for heating runs similar to that expected for a field of 180 V cm^{-1}, while the data for cooling runs are practically the same as those for $E = 0$.

For a low applied field and at a low temperature variation rate, the effective field is found to be weaker for cooling runs from the paraelectric phase than for heating runs. Nevertheless, the effective field for the cooling runs goes to the heating run values (equilibrium values) as the measurements are carried out at an extremely low temperature variation rate.

This fact may be related to kinetic differences that occur in setting the effective field. When cooling under an applied electric field, a long time is required to reach the equilibrium value of that effective field. In this sense, it has been suggested previously that the nucleation process and the resulting domain pattern are sensitive to the temperature variation rate [11, 12].

Since specific heat is a macroscopic property, it would be interesting to correlate these measurements with other experiments related to microscopic properties, such as a visualization of domain wall movement, to understand the causes that induce the effective field. Nevertheless, the temperature resolution of this kind of experiment could make it very difficult to appreciate what happens in such a small temperature interval (0.2 K) around the transition temperature.

Acknowledgments

This work was supported by project BFM2002-02237 of the Spanish DGICYT. The authors wish to thank Professor M Koralewski for making the sample available and Professor José María Martín Olalla for his contribution to the preparation of this manuscript.

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