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2005 J. Phys.: Condens. Matter 17 5001

(http://iopscience.iop.org/0953-8984/17/33/005)

INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **17** (2005) 5001–5010 doi:10.1088/0953-8984/17/33/005

Specific heat of ferroelectric TGSe under electric field: analysis in terms of Landau theory

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Received 4 May 2005, in final form 22 June 2005
Published 5 August 2005
Online at stacks.iop.org/JPhysCM/17/5001

Abstract

The specific heat of the ferroelectric–paraelectric phase transition in TGSe under several electric fields in the range 175–750 V cm^{-1} has been measured and analysed in terms of the same tricritical Landau potential obtained at zero electric field plus the term $-\xi Q$, which represents the simplest form to include the coupling between the order parameter Q and the electric field E ($\xi \propto E$). Data in the ferroelectric phase have been successfully fitted and it has been found that $\xi = k(E + E_0)$, where k is constant and $E_0 \sim 150$ V cm^{-1}. It has been found that in order to describe the behaviour in both phases simultaneously it is necessary to consider a more complex coupling between the electric field and the order parameter, which makes the critical temperature and the coefficient of Q^6 in the tricritical potential be renormalized by the field.

1. Introduction

Triglycine selenate [$(NH_2CH_2COOH)_3H_2SeO_4$], hereafter TGSe, is a well-known uniaxial ferroelectric material belonging to the triglycine sulfate (TGS) family. It 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 recent paper [3], we analysed the phase transition in a high-purity sample of TGSe by calorimetric measurements. No latent heat was detected, indicating that the phase transition is continuous, and the specific heat of the ferroelectric phase was found to follow a classical tricritical Landau potential, $\Delta G = \frac{1}{2}A\varepsilon T_c Q^2 + \frac{1}{6}C Q^6$; Q is the normalized order parameter, $Q = \frac{P}{P_0}$, P is the polarization and P_0 is the spontaneous polarization at $T = 0$ K, so that Q varies from zero in the paraelectric phase to the unity at 0 K; ε is the reduced temperature given by $\varepsilon = \frac{T-T_c}{T_c}$ 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.

The tricritical nature of this phase transition makes it very interesting to study the effect of external fields and defects on the properties of TGSe, since small perturbations shift the

transition to first or second order. Different experiments have been performed to analyse these effects. Hydrostatic pressure and deuteration makes the transition first order [4–6] and a tetracritical point has been established at a hydrostatic pressure of 2.3 kbar and at a deuterium concentration of 38% [7]. The introduction of defects by γ irradiation shifts the transition to second order [8]. In the case of the experiments under uniaxial stress, different results have been found depending on the direction along which it has been applied. If the uniaxial stress is applied along the a axis the transition remains near the tricritical point, whereas if it is applied along the b (ferroelectric axis) and c axes the second-order phase transition character is strengthened [9]. These results were recently confirmed by calorimetric measurements [3], where we found that a weak uniaxial stress of 10 bar along the ferroelectric axis shifts the transition to second order.

On the other hand, the study of a ferroelectric phase transition under an external electric field E has a special interest, since it is the field conjugated to the polarization. Fugiel and Mierzwa [10] investigated the isothermal behaviour of the electrical susceptibility as a function of electric field for $E < 10\ \mathrm{kVcm}^{-1}$ in the ferroelectric and paraelectric phases. The results indicate that a different equation of state may exist for each phase. The data for the ferroelectric phase for $T < T_c - 0.5$ K were found to fulfil a classical tricritical Landau equation of state, where the coefficients of the Landau expansion A, C and T_c were assumed to be independent of the electric field. In that paper a non-Landau behaviour of the data in the paraelectric phase is also suggested.

The scaling equation of state which relates the polarization and the electric field has also been successfully investigated from hysteresis loop measurements [11], in terms of the generalized effective field approach developed by Gonzalo [12], which asymptotically gives the classical Landau theory at $T = T_c$.

On the other hand, the determination of the specific heat under electric field in the neighbourhood of a ferroelectric phase transition is very interesting because it provides a way to study the energetic effect of the electric field on the phase transition. In addition, the applicability of TGSe as a pyroelectric detector makes it very interesting to determine the specific heat near the transition temperature because it is one of the variables which define the pyroelectric figure of merit.

The specific heat of the ferroelectric phase transition in TGSe under electric field has been previously studied for $E > 500\ \mathrm{V\ cm}^{-1}$ [13]. It was found that the effect of the field was to reduce the anomaly and to broaden it to higher temperatures. Nevertheless, no analysis in terms of Landau theory was performed either in the ferroelectric or in the paraelectric phase.

The analysis of the effect of the electric field on the phase transition in terms of a theoretical model, like Landau theory, requires characterizing very well the behaviour near the transition temperature where the difference between data under different electric fields is high enough to be investigated. This fact makes it necessary to use a technique which provides a high number of experimental points in that region and which allows applying an external electric field without disturbing the measurement.

The aim of the present paper is to investigate the influence of the electric field on the phase transition in TGSe by specific heat measurements using conduction calorimetry. The experimental device [14], designed and built by the group, permits studying the effect of uniaxial stress and electric field on both the specific heat and the latent heat. It has allowed characterizing experimentally and theoretically various phase transitions under external fields. In the case of ferroelastic $KMn_{1-x}Ca_xF_3$, from the analysis of the specific heat, a 2-4-6 Landau potential was determined as suitable to describe very precisely the effect of the doping on the phase transition [15]. This technique was also used to study the effect of an electric field on the ferroelectric phase transition in TGS [16] and to investigate the applicability of a 2-4 Landau

potential under field, and a qualitative agreement between the theoretical predictions and the experimental data was found.

The specific heat data will be analysed in terms of the classical Landau theory. We consider initially that the only effect of the field is to add a $-\xi Q$ term to the Landau potential determined for zero electric field [3], where ξ represents the field conjugated to the order parameter. In this frame, only the specific heat data in the ferroelectric phase are well described. To describe the specific heat in both phases, it is necessary to consider that the transition temperature and the coefficient of Q^6 are renormalized by the action of the field.

2. Experimental details

The sample of TGSe, a parallelepiped with a thickness of 2.72 mm and an area of 55 mm^2, was prepared at the Institute of Physics, Adam Mickiewicz University, Poznan (Poland). It was grown from aqueous solution by slow evaporation of water at constant temperature above the Curie point. The crystal obtained was colourless and of high optical quality. The ferroelectric axis, *b*-axis, of the single crystal was determined by the cleavage plane (010). The main faces were prepared perpendicular to the *b*-axis and gold electrodes were evaporated on them.

The calorimetric measurements were performed by means of a high-resolution conduction calorimeter, which has been described in detail in [14]. The sample is pressed between two identical heat fluxmeters, which are made from 50 chromel–constantan thermocouples [17] connected in series with the wires placed in parallel lines. One of the fluxmeters is fixed to a calorimeter block while the other is pressed by a bellows. The fluxmeters, which have a cross-section of 1 cm^2, are rigid enough to apply a controlled uniaxial stress on the sample in the range between 0 and 20 bar. Two electrical resistances and two electrodes are placed between each face of the sample and fluxmeters. The resistances can dissipate a uniform heat power on the sample faces and the electrodes allow for applying an electric field in the sample.

The entire assembly is placed in a cylindrical hole made in a cylindrical piece of bronze (10 kg) which serves as the heat sink (the calorimeter block). Its temperature is measured with a commercial platinum thermometer and a resistance bridge. The block and two surrounding radiation shields are placed into an hermetically sealed outer case under vacuum (10^{-7} Torr).

This high vacuum together with the small difference of temperature between the sample and the calorimeter block (lower than 5×10^{-2} K) avoids lateral heat losses and it ensures a unidimensional heat conduction through the fluxmeters. The calorimeter is placed in an automatically controlled thermostat. The large thermal inertia of the calorimeter allows the block to have a very good thermal stability. These features, together with the high number of thermocouples, make the device highly sensitive. As a result, it is possible to measure the specific heat changing the temperature of the assembly at a rate even lower than 0.1 K h^{-1} without observing significant temperature fluctuations in the block temperature.

The specific heat is measured using the method previously described in [18]. The same constant power is dissipated in both heaters for 12 min to reach a steady state characterized by a constant temperature difference between the sample and the calorimeter block. The power is then cut off until a new steady state is reached again. Then, the power is switched on again and the sequence is continuously repeated while the temperature of the assembly is changed at a low constant rate. The integration of the electromotive force given by the fluxmeters between every pair of steady state distributions allows us to determine the thermal capacity of the sample. On account of the low temperature scanning rate, one experimental point is obtained approximately every 0.01 K, allowing precise characterization in the neighbourhood of the phase transition.

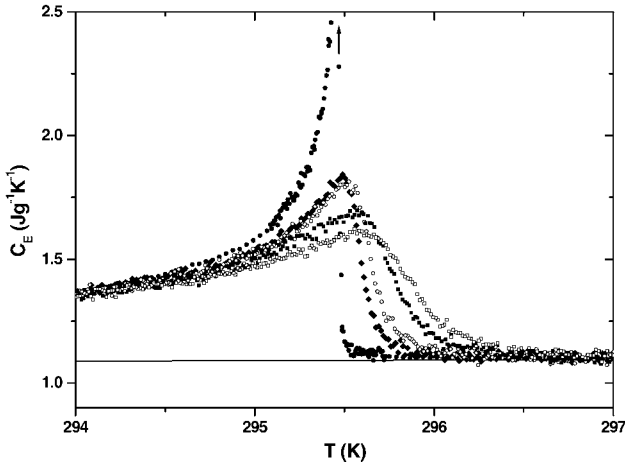

Figure 1. Specific heat of TGSe for $E = 0$ (full circles), 175 V cm^{-1} (full diamonds), 250 V cm^{-1} (open circles), 500 V cm^{-1} (full squares) and 750 V cm^{-1} (open squares). The baseline determined in [3] is also included.

3. Results

The specific heat of TGSe under several electric fields ($E = 175, 250, 500, 750$ V cm^{-1}) was measured, heating and cooling the sample at 0.03 K h^{-1}. Each electric field was applied when the temperature was 10 K above the transition temperature and it was kept constant during the cooling and heating runs. The measurements were performed on the same sample and at the same temperature scanning rate used in the previously reported investigation at zero electric field [3], so that the data are directly comparable. No difference was found between the heating and cooling data for each field.

The specific heat data for each field are represented in figure 1 together with the specific heat for $E = 0$ and the baseline used to calculate the specific heat excess, determined in [3]. As is well known, the effect of the electric field is to decrease the anomaly and to broaden it to higher temperatures, making the tail at higher temperatures become more significant. These results are in agreement with previously reported results for higher values of the electric field [13].

We will investigate if the above data are described by a classical tricritical Landau potential. We assume initially that the coefficients A, C and T_c are the corresponding ones for the zero electric field data whose values were determined previously [3] and indicated above. We also assume that the effect of the electric field is included by means of a term $-\xi Q$ in the power expansion, where ξ represents the electric field (note that Q is dimensionless, so ξ is in units of energy). This introduction of the electric field is the simplest one found in the literature and it is analogous to that made previously in the analysis of the dielectric susceptibility [10]. The corresponding equation of state is given by

$$\xi = AT_c\varepsilon Q_{eq} + CQ_{eq}^5. \tag{1}$$

Q_{eq} has to be calculated numerically from the equation of state at every temperature since the explicit dependence in terms of ε and ξ cannot be written.

The specific heat excess in an electric field ΔC_E follows the relation

$$\Delta C_E = -A(1+\varepsilon)Q_{eq}\frac{dQ_{eq}}{d\varepsilon}. \tag{2}$$

Table 1. Fitted fields ξ obtained from the fit of ΔC_E in electric fields for $T < T_c$ using the tricritical Landau potential for TGSe at zero electric field plus the term $-\xi Q$.

E (V cm^{-1})	$\xi \times 10^{-3}$ (J g^{-1})
175	1.56
250	1.92
500	3.13
750	4.33

Since Q_{eq} cannot be explicitly written in terms of ε and ξ, it is not possible to get an analytical expression for ΔC_E as a function of ξ and ε. It is possible to solve this problem if we work with the theoretical expression $\Delta C_E(Q_{eq}, \xi)$, obtained by including $\varepsilon(Q_{eq}, \xi)$ and $\frac{dQ_{eq}}{d\varepsilon}$ from (1) in (2):

$$\Delta C_E(Q_{eq}, \xi) = -A\,Q_{eq}\frac{1 + \frac{\xi}{AT_c}\frac{1}{Q_{eq}} - \frac{C}{AT_c}Q_{eq}^4}{-\frac{\xi}{AT_c}\frac{1}{Q_{eq}^2} - 4\frac{C}{AT_c}Q_{eq}^3}. \tag{3}$$

The experimental data to fit are ΔC_E at each temperature, $\Delta C_E(\varepsilon)$. Taking into account that the coefficients A, C and T_c are assumed to be independent of field, the only fitting parameter is the field ξ. We indicated above that it is not possible to obtain explicitly the analytical dependence $\Delta C_E(\varepsilon, \xi)$, so we have programmed a fitting routine, based on the analysis of equations (1) and (3).

The first step is to select an experimental point Δc_E at one temperature. Since the equilibrium order parameter Q_{eq_i} is normalized and varies from 0 to 1 ($Q_{eq} \in (0, 1)$), the routine partitions this interval into a set of discrete values Q_{eq_i} very close each other. The number of values for Q_{eq_i} is taken as high as possible to minimize the uncertainty in the fitting procedure. At each Q_{eq_i}, the fitting parameter ξ is varied in small steps and $\Delta C_E(Q_{eq_i}, \xi_i)$ is calculated from (3) and its corresponding reduced temperature ε_i from (1), so that $\Delta C_E(\varepsilon_i, \xi_i)$ is numerically obtained. The comparison of the selected experimental point ΔC_E with the set of values calculated using the routine provides the parameter ξ_i which best fits that experimental point. The process is then repeated for all the data, in such a way that ξ_i is obtained for each experimental point. If this model is suitable for explaining the experimental data, the whole temperature dependence of the specific heat should be described with the same fitting parameter and, then ξ_i should be, within the statistical uncertainty, the same. Otherwise, the interval where ξ_i varies indicates the region where this model is not fulfilled.

For each electric field, the specific heat data for $T < T_c$ were successfully fitted with an average parameter ξ, whose value for each electric field is summarized in table 1. In figure 2, we have plotted ΔC_E versus T together with the theoretical curves corresponding to the fits, showing a very good agreement for $T < T_c$.

In figure 3, we plot the parameter ξ which fits the specific heat data for $T < T_c$ versus the external electric field. ξ shows a linear dependence on the electric field which does not cross the abscissa at the origin. It seems to suggest that the field ξ in the model is related to the external electric field as $\xi \propto (E + E_0)$ where $E_0 \sim 150$ V cm^{-1}. This indicates that in order to fulfil the model, it is necessary to consider that the field ξ conjugated to the order parameter is not directly proportional to the external field but it is corrected by an additional constant contribution E_0. This contribution does not seem to be associated with an intrinsic internal bias field since the hysteresis loop was found to be symmetrical and the specific heat data measured with the electric applied in the opposite direction show the same behaviour.

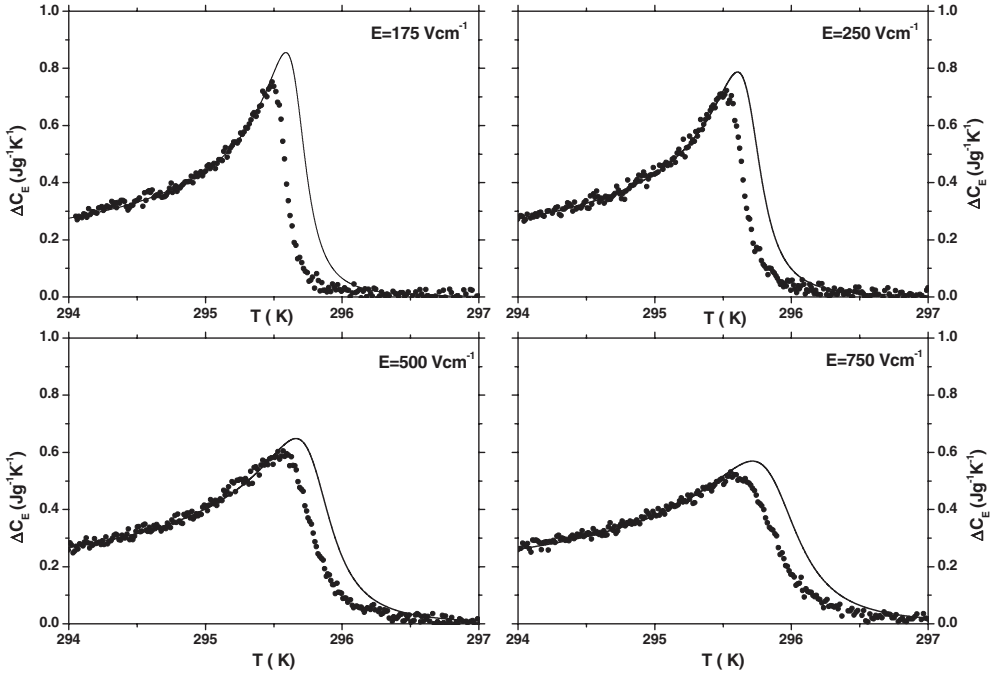

Figure 2. Specific heat excess in electric fields for $E = 175$, 250, 500 and 750 V cm^{-1}. The lines represent the best fit for $T < T_c$ using the model which takes the Landau tricritical potential determined in [3] plus a term $-\xi Q$.

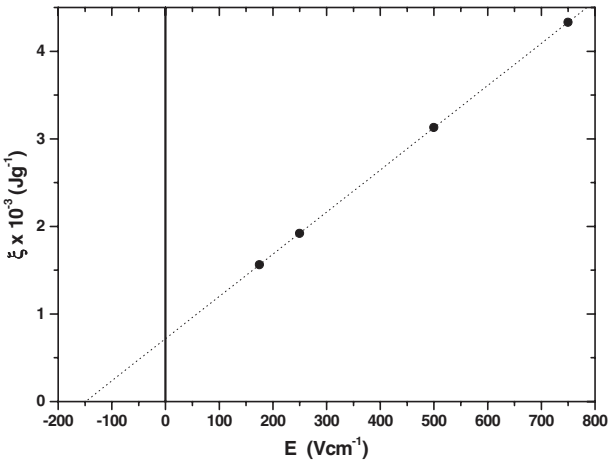

Figure 3. Fitted ξ for $T < T_c$ versus the applied electric field. ξ enters the Landau tricritical potential as a term $-\xi Q$.

Fugiel and Mierzwa [10] investigated the electrical susceptibility in terms of a Landau tricritical potential analogous to that which we have used. In their study the field conjugated to the order parameter is directly the external electric field while in our case an additional contribution E_0 arises. The reason for this difference could be related to the fact that both studies have been performed focusing the fitting in different temperature intervals. In [10], the

region nearer to the phase transition, where the anomaly is bigger, was discarded and the fit was only made for $T < T_c - 0.5$ K. It was suggested that the investigation in the immediate neighbourhood of the phase transition is complicated because the susceptibility does not tend to infinity and the spontaneous polarization does not go to zero at the transition temperature due to different effects such as surface layer effects, inhomogeneities in the sample and local electric fields present even in the paraelectric phase.

Nevertheless, the difference between the specific heat values in various electric fields is more significant when the transition temperature is approached and decrease rapidly far from the transition. Our study has been performed including the data around the specific heat maximum which have been found to be reproducible in different experiments. If we used the potential determined in [10], the specific heat behaviour would be explained until $T < T_c - 0.5$ K, but it would not explain the region nearer T_c, which is the most significant on account of its magnitude.

From the analysis in terms of this model, it can be concluded that, very close to the transition temperature, the field conjugated to the order parameter is not directly the external field E. We must include an internal field contribution E_0 which has to be taken into account to describe the dynamical behaviour of the material in the region where the sample changes from one phase to the other and the polarization changes very rapidly.

On the other hand, for $T > T_c$, the parameter ξ which fits the experimental data for each field is found to be temperature dependent, indicating that it is not possible to find a fitting field ξ which simultaneously describes data for both the ferroelectric and paraelectric state. This fact suggests that, in this region, the internal field is strongly affected by the above-mentioned effects and data in the paraelectric phase cannot be described in terms of this simple Landau model as it is generally accepted in the literature. This result is also in agreement with the dielectric susceptibility analysis [10].

The internal field can be related to the previously reported idea that the effective field on the sample is the external field plus different terms depending on successively higher-order terms in the polarization, which can be attributed to dipolar, quadrupolar, octopolar, etc contributions [19]. It has been shown [11] that in the case of the tricritical phase transition in TGSe the derived equation of state is analogous to the corresponding one derived above from Landau theory (equation (2)) but it contains specific temperature dependence for the Q^5-coefficient. Nevertheless, in the temperature interval under investigation ($294 < T < 297$, where the anomaly in the specific heat is significant), the variation of the coefficient of Q^5 with temperature is lower than $\pm 1.5\%$, so it can be considered practically temperature independent.

To improve the above analysis including the data in the paraelectric phase and to keep an equation of state similar to (2), which is compatible with the effective field approach, we assume that the coefficients T_c^* and C^* become different to the corresponding ones for the zero electric field data T_c and C. This may be a consequence of higher coupling terms between ξ and Q ($\xi^m Q^n, m, n > 0$) which could be allowed in the Landau expansion [20]: the terms which include Q^2 renormalize T_c and the terms which include Q^6 renormalize C. In any case, to obtain an equation of state analogous to the one which arises from the effective field approach, it is necessary that the interaction energy between the field and the order parameter involves the same powers of Q as the Landau potential does. The corresponding Landau potential is

$$\Delta G = \tfrac{1}{2} A T_c^* \varepsilon Q^2 + \tfrac{1}{6} C^* Q^6 - \xi^* Q.$$

Consequently, it would be interesting to fit the specific heat data to a potential of these characteristics. The procedure to fit the experimental data $\Delta c_E(T)$ to this model gets more complex because the number of fitting parameters has increased (T_c^*, C^* and ξ^*). Nevertheless, from the equation of state (1) and using the well-known relation between the entropy excess ΔS

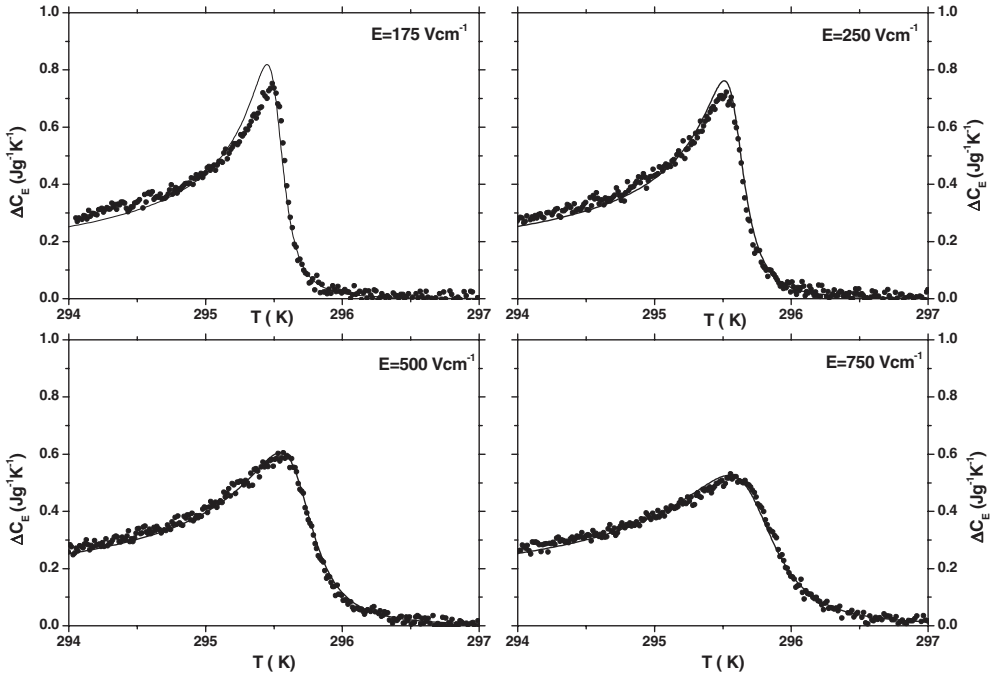

Figure 4. Specific heat excess in electric fields for $E = 175$, 250, 500 and 750 V cm^{-1}. The lines represent the fit of the Landau potential where the coefficients are renormalized as a consequence of the electric field effect.

Table 2. Coefficients of the renormalized Landau potential.

E (V cm^{-1})	T_c^* (K)	$\xi^* \times 10^{-3}$ (J g^{-1})	C^* (J g^{-1} K^{-1})
175	295.37	1.15	31.6
250	295.42	1.44	30.2
500	295.38	2.80	29.0
750	295.32	4.16	28.2

and the order parameter, $\Delta S = -\frac{1}{2} A Q_{\mathrm{eq}}^2$, it is possible to get an analytical expression for the temperature as a function of ΔS and the field:

$$T = T_c^* + \frac{\xi^*}{A}\left(\frac{A}{2\Delta S}\right)^{1/2} + \frac{C^*}{A}\left(\frac{2\Delta S}{A}\right)^2.$$

To fit the model, it is necessary to fit the experimental data for the temperature T versus the entropy excess ΔS, where C^*, T_c^* and ξ^* are the fitting parameters.

The temperature dependence of the entropy excess can be obtained experimentally by the numerical integration of the specific heat excess data $\Delta S = \int \frac{\Delta C_E}{T}\,\mathrm{d}T$. The advantage of our technique is that the high number of available experimental data for ΔC_E allows for making the integration very precisely.

The least-squares fitting routine yielded the theoretical curves represented in figure 4 and the values of the parameters summarized in table 2. The theoretical prediction of this model provides an adequate description of the data below and above T_c, although the fit for $E = 175$ V cm^{-1} is not as good as those obtained for higher electric fields.

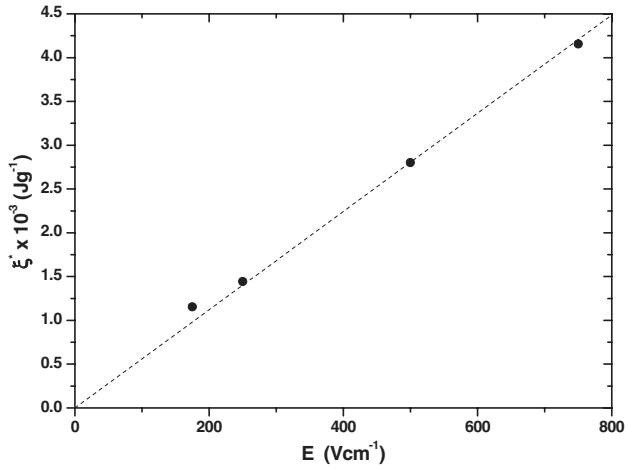

Figure 5. Fitted ξ versus applied electric field E when the coefficients are renormalized due to the effect of the electric field.

In figure 5, we represent the determined field ξ^* versus the electric field E. The data except for the lowest electric field show a linear tendency, which crosses the abscissa at the origin. This indicates that the parameter ξ^* is, in this case, strictly proportional to the external electric field, $\xi^* = kE$. Now, the effect of the internal field is included in the renormalization of the coefficients of the Landau potential.

Concerning the other fitting parameters, C^* and T_c^* are found to be very similar for each field. While C^* is found to be 29 ± 1 J g^{-1} K^{-1}, higher than the determined value for $E = 0$ ($C = 24$ J g^{-1} K^{-1}), T_c^* decreases about 0.15 K with respect to the value determined at zero electric field.

As a conclusion, it has been found that the specific heat excess of TGSe in electric fields can be interpreted in terms of Landau theory, even very near to the transition temperature. The first model puts in evidence the existence of an internal field and the impossibility of fitting the data in the paraelectric phase. The second model, which implies a more complex coupling between the field and the order parameter, includes this internal field in the renormalization of the transition temperature and the coefficient of Q^6 in the Landau potential and it allows for describing the specific heat behaviour in the paraelectric phase.

Acknowledgments

This work has been supported by project BFM2002-02237 of Spanish DGICYT. The authors wish to thank Professor J A Gonzalo for fruitful conversations and Professor M Koralewski for making the sample available.

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