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Evidence of Landau tricritical behaviour in TGSe by calorimetric measurements: effect of a weak uniaxial stress

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Abstract

The paraelectric–ferroelectric phase transition of a single crystal of triglycine selenate TGSe, whose first- or second-order character is controversial, has been studied using a high sensitivity calorimetric technique. The specific heat of a highly pure TGSe has been measured and no evidence of latent heat has been found. The anomalous part of the specific heat shows Landau tricritical behaviour. Experimental data have been fitted to a 2–6 Landau potential, whose coefficients have also been obtained. A weak uniaxial stress applied along the ferroelectric axis (10 bar) decreases the anomalous part of the specific heat. This effect is different for cooling and heating runs. The equilibrium data are those obtained on heating that fit to a 2–4–6 Landau potential, which indicates that the transition shifts to second order with the effect of uniaxial stress.

1. Introduction

Triglycine selenate ($(NH_2CH_2COOH)_3H_2SeO_4$), hereafter TGSe, is a well known uniaxial ferroelectric material 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]. Although the continuity of the phase transition in TGS has been confirmed in many experiments, the results of analogous measurements in TGSe have been interpreted ambiguously. Although the transition has been considered traditionally second order near a tricritical point [3, 4], recently, from thermal hysteresis in dielectric constant measurements, there has been suggested a slightly first-order character but very near to a tricritical point [5]. Nevertheless the latent heat of this crystal has not been investigated.

Different experiments have been carried out to induce tricritical behaviour by application of hydrostatic or uniaxial pressure, by deuteration of the sample or γ-irradiation. The coefficients of a 2–4–6 Landau potential [3, 4] have been calculated. For pure TGSe, a non-zero value of B, prefactor of Q^4, has always been found and attempts have been made to find the experimental conditions (hydrostatic or uniaxial stress, deuteration or γ irradiation) that make B equal to zero (tricritical point).

In this sense, deuteration makes the transition first order [6, 7] and a tetracritical point is established at a hydrostatic pressure of 2.3 kbar and at a deuterium concentration of 38% [8].

When uniaxial pressure [4] is applied along the b (ferroelectric axis) and c axis the second-order phase transition character is strengthened, whereas if it is applied along the a^* axis the transition keeps near the tricritical point. In this last case, it has been estimated that the tricritical point is achieved for a critical pressure equal to 600 bar [4], although this stress has not been applied due to the mechanical damage which it would cause to the sample.

On the other hand, from electric susceptibility measurements, Fugiel and Mierzwa [9] found a Landau tricritical equation of state under very high electric fields, which provides a good description for the ferroelectric phase at temperatures below $T_c - 0.5$ K. Nevertheless, this equation is not fulfilled near the transition temperature nor in the paraelectric phase.

The controversial about the nature of the phase transition arises due to the fact that the transition takes place in a really short temperature interval, 0.5 K, which makes the experimental definition of physical properties that characterize the phase transition, such as specific heat or dielectric constant, around the transition point very difficult. Also the measurement of a low latent heat when the specific heat presents an important anomaly is a very complicated experimental problem as we will analyse below.

The specific heat of TGSe has been reported previously [10–13]. The specific heat obtained by ac calorimetry [11] presents a strong anomaly at the transition temperature. The data showed a small tail above the transition temperature which shows a logarithmic behaviour. This logarithmic anomaly is observed in a range of 10–20 K above T_c.

Strukov *et al* [13] have also obtained the specific heat behaviour of TGSe and have studied the influence of an electric field. For zero electric field, the specific heat presents an anomaly, that it is found to be bigger than that expected for a second-order Landau behaviour. Nevertheless, no analysis in the frame of Landau tricritical behaviour is achieved.

Song *et al* [3] analyse, in the frame of a 2–4–6 Landau potential, the specific heat behaviour of TGSe and DTGSe with 62% of deuterium, under different doses of γ-irradiation. For pure TGSe they obtained a non-zero coefficient of Q^4 which increases when the γ-irradiation dose increases, while the coefficients of Q^2 and Q^6 keep practically constant. For a DTGSe crystal with 62% of deuterium they obtained a tricritical phase transition for a small dose of D = 0.3 MR. No measurement of latent heat was achieved.

In this work, we will characterize the paraelectric–ferroelectric phase transition of TGSe by latent heat and specific heat measurement.

The measurements of latent heat very close to the tricritical point present two difficulties: (a) the latent heat must be very small, if it is present, and (b) the specific heat c must show a great anomaly; for instance, the Landau theory predicts a divergence of c_p at the transition temperature. On the other hand, the traditional methods for determining the latent heat (differential scanning calorimetry (DSC), differential thermal analysis (DTA), etc) really measure changes of enthalpy. This change of enthalpy has two contributions: one due to the specific heat variation with the temperature and another due to the latent heat. The experimental method must separate both contributions.

Our group has developed an original method [14], named *square modulated differential thermal analysis*, based on conduction calorimetry, to investigate the first-order character of

a phase transition and to evaluate the latent heat, if it is present. A series of long-period square thermal pulses is superposed on a heating or cooling ramp. The samples pass from a uniform temperature distribution to another one and the integration of the electromotive force (emf), given by the fluxmeters between both temperature distributions, allows us to determine absolute values of the specific heat of the sample.

We can carry out a second run with the same temperature ramp but without modulation, in such a way that the equipment works as a very sensitive DTA device. As both sets of data, DTA trace and specific heat, are obtained with the same device, on the same sample and under similar thermal conditions, it is possible to compare them. The high number of thermocouples forming the fluxmeters allows the device to work at a very small temperature scanning rate, less than 0.1 K h^{-1}. From the specific heat data, we calculate the DTA trace which would correspond exclusively to the thermal capacity contribution. The latent heat is present in the temperature interval where the measured and the calculated DTA traces do not coincide. Obviously, when both coincide, the transition is considered to be continuous.

This technique has been applied to the study of the almost tricritical phase transition of $KMnF_3$ [15], whose latent heat was first measured with this technique. Furthermore, the effect of the substitution of Mn by Ca was also successfully investigated measuring the latent heat [15–17], which showed that the doping makes the transition shift to second order. This method has also been applied to show that the phase transition in CoO [18], whose character was controversial, is continuous.

In this work we will apply this technique to show that no latent heat is found for TGSe and to obtain very precise specific heat measurements which will show that this phase transition is just at the tricritical point. The Landau coefficients will be calculated and the effect of a very weak uniaxial stress applied along the ferroelectric axis on the phase transition character will be also investigated.

2. Landau tricritical behaviour

Phase transition behaviour and its nature near the tricritical point, which is an intersection of three critical lines in a three-dimensional thermodynamic space, are described by Landau's phenomenological theory. The Landau theory is based on an expansion of the free energy ΔG in terms of the order parameter Q, which takes near the tricritical point terms until Q^6 [19]:

$$\Delta G = \tfrac{1}{2}A(T - T_c)Q^2 + \tfrac{1}{4}BQ^4 + \tfrac{1}{6}CQ^6$$

where T_c is the transition temperature, and A, B and C are temperature independent coefficients. For a second-order phase transition close enough to the tricritical point, B is positive but C is not negligible compared to B. In a ferroelectric phase transition the order parameter is the spontaneous polarization P and it is convenient to define a normalized order parameter $Q = \frac{P}{P_s^0}$, where $P_s^0 = P(T = 0\ \mathrm{K})$.

At a tricritical point the prefactor of Q^4, B, is zero, so that a 2–6 Landau potential is obtained. We will consider the case of second order or tricritical phase transitions.

The equilibrium order parameter is obtained from the condition $(\partial \Delta G/\partial Q)_{Q=Q_{eq}} = 0$, which implies that the order parameter falls continuously to zero at $T = T_c$ as

$$Q_{eq}^2 = \frac{-B + \sqrt{B^2 - 4AC(T - T_c)}}{2C}, \qquad \text{if } B = 0 \qquad Q_{eq}^4 = \frac{-A(T - T_c)}{C}.$$

In both cases, the specific heat takes the form [20]

$$\Delta c = \left(\frac{A^3}{16C}\right)^{1/2} \frac{T}{(T_2 - T)^{1/2}} \tag{1}$$

where

$$T_2 = T_c + \frac{B^2}{4AC}. \tag{2}$$

For a second-order phase transition, T_2 is the temperature where the specific heat would diverge but it is not thermodynamically accessible, since the highest temperature at which the ferroelectric phase is stable is T_c. In the limit where $B = 0$, $T_2 = T_c$ and the tricritical point is obtained. The coefficient $\frac{B^2}{4AC}$ shows the temperature difference between T_2 and T_c and it indicates the proximity to the tricritical point. Nevertheless, it is more convenient to use a dimensionless quantity and take into account the possibility that we may need to compare systems with different transition temperatures. Thus, the quantity $K = \frac{B^2}{4ACT_c}$ is preferable as a measure of the closeness to tricriticality of a phase transition.

The analysis of the experimental specific heat data through equation (1) provides an excellent way to determine whether a phase transition follows the predictions of Landau theory. Nevertheless, to obtain reliable conclusions the specific heat data must be very precise to define the shape of the anomalous part near the transition point.

Experimentally, when the transition is sharp, we can assume that T_c is the temperature of the maximum of the specific heat. If we represent $(T/\Delta c)^2$ versus T, we can fit a linear regression to experimental data; following equation (1) $(16C/A^3)$ is the slope and T_2 is the intersection with the abscissa. If the difference between T_2 and T_c is within our experimental resolution for temperature, we can considerer that $T_2 = T_c$ and the phase transition can be considered tricritical; in another case, $T_2 - T_c$ gives the value of B from equation (2).

Finally, the last condition to obtain the coefficients A, B and C is by imposing that the order parameter Q is unity at $T = 0$ K.

3. Experimental details

The sample of TGSe was prepared at the Institute of Physics, Adam Mickiewicz University, Poznan (Poland). It was a parallelepiped with a thickness of 2.72 mm and an area of 55 mm^2.

Single crystals of TGSe were grown from aqueous solution by slow evaporation of water at constant temperature above the Curie point. The crystals obtained were 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.

The measurements of the heat flux and specific heat were performed by means of high resolution conduction calorimetry, which has been described in detail [21]. The sample is pressed between two identical heat fluxmeters, which are made from 50 chromel–constantan thermocouples [22] connected in series with the wires placed in parallel lines. Two electrical resistances are placed between each face of the sample and fluxmeters. These resistances can dissipate a uniform heat power on the sample faces.

One of the fluxmeters is fixed to the calorimeter block while the other one is pressed by a bellows. The bellows is connected through a capillary to an outer pressure bottle of N_2-50. An array of valves allows us to control the gas pressure in the bellows or to create vacuum in it. The force transmitted by the bellows has been calibrated [21] as a function of the gas pressure in it and the accuracy of the applied stress is estimated to be 0.1 bar. The mechanical consistence of the fluxmeters, which have a cross section of 1 cm^2, allows us to apply a controlled uniaxial stress on the sample in the range between 0 and 20 bar. Nevertheless, the very different cross sections of the fluxmeters (1 cm^2) and the sample (0.55 cm^2) make it not recommendable to apply a uniaxial stress bigger than 10 bar, to avoid any mechanical damage to the fluxmeter.

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 in a 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 heat flux changing the temperature of the assembly at a rate as low as 0.01 K h^{-1} without observing significant temperature fluctuations (always less than 10^{-6} K) in the block temperature.

The specific heat is measured using the method previously described [14, 23]. The same constant power W is dissipated in both heaters (dissipation branch) 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 (relaxation branch). 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. That is, a long-period series of square thermal pulses is superposed to a heating or cooling ramp. The integration of the electromotive force V given by the fluxmeters between every pair of steady state distributions allows us to determine the thermal capacity of the sample. We must point out that we obtain two c data in each cycle: one from the dissipation branch (c_d) and another from the relaxation branch (c_r). Specific heat data obtained in the dissipation and relaxation semiperiods of every square pulse show a regular behaviour if there is no phase transition or if it is second order. If a first-order phase transition takes place, both data become very different and show an anomalous behaviour in the temperature interval where the latent heat is produced, indicating the discontinuous character [14].

On the other hand, the DTA trace is continuously measured in a second run without dissipation in the sample and using the same temperature scanning rate as used to measure the specific heat. The equipment works like a very sensitive DTA device. The electromotive force given by the fluxmeters is proportional to the heat flux, Φ_D, exchanged between the sample and the calorimeter block.

From the specific heat data obtained in the first run and using the previously described method [14, 15], we calculate the heat flux Φ_c which would correspond exclusively to the thermal capacity behaviour around the transition temperature. The effect of the latent heat is present in the temperature interval where Φ_D and Φ_c do not coincide. The integration of Φ_D in that temperature interval allows us to calculate the latent heat. The sensitivity of this method is estimated to be better than 0.001 J g^{-1}, even when the specific heat shows a strong anomaly in the transition.

4. Results

4.1. Specific heat and latent heat for TGSe at $\sigma = 0$

Following the described method the temperature dependence of the specific heat (c_p) of TGSe was measured in different runs cooling and heating the sample. The experiments were carried out on quasistatic conditions at a scanning temperature rate of ± 0.1 K h^{-1}, except near the transition temperature where the temperature variation rate was ± 0.03 K h^{-1} to determine precisely the anomaly of the specific heat (a point of specific heat is obtained every 0.006 K in

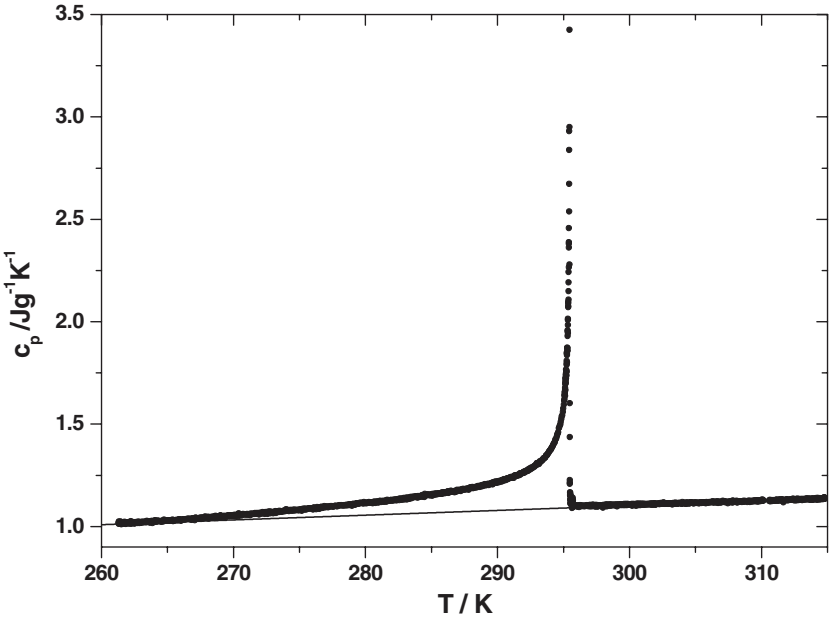

Figure 1. Specific heat of TGSe versus T in a wide temperature interval on cooling and heating at 0.1 and 0.03 K h^{-1} near the transition. The baseline for the regular part of specific heat is also represented.

this interval). The temperature increment of the sample during the measurement process ΔT is evaluated to be 0.01 K near the transition temperature. In figure 1, we represent the specific heat data in a wide temperature range. This specific heat shows a linear temperature dependence in the paraelectric phase and a sharp λ-type anomaly around the transition temperature ($T_{max} = 295.46$ K). The maximum of the specific heat decreases by approximately 80% of its value in 0.5 K. The data agree with those found in [13], but the peak is more pronounced, which could be due to the high quality of the sample together with the quasistatic temperature variation and the small increase of temperature during the measurement. Both sets of data, cooling and heating, coincide and no thermal hysteresis is found.

In figure 2, we have plotted the specific heat excess obtained in the dissipation branch (c_d) and in the relaxation branch (c_r). We observe that both sets of data show the same temperature dependence. We have reported previously [14] that when a first-order phase transition takes place, c_d and c_r become very different in the temperature interval where the latent heat is produced. The difference is notorious even in systems near the tricritical point, where the latent heat is very small ($L = 0.13$ J g^{-1} for $KMnF_3$, $L = 0.010$ J g^{-1} for $KMn_{0.997}Ca_{0.003}F_3$) [14]. In the case of TGSe, the similar behaviour of c_d and c_r seems to indicate that no trace of latent heat is present.

To confirm this last suggestion, we measured the DTA trace in a second run, changing the temperature of the sample at the same constant rate as used in the specific heat measurements to make both sets of data comparable. We must point out that the used temperature variation rate is about two orders of magnitude lower than the minimum value allowed in conventional DTA equipments. In figure 3, we represent the heat flux given by the fluxmeters Φ_D (DTA trace) and the heat flux Φ_c, calculated from the specific heat data using the previously described method, for the cooling and heating runs. We must point out that the heat flux, due to phase

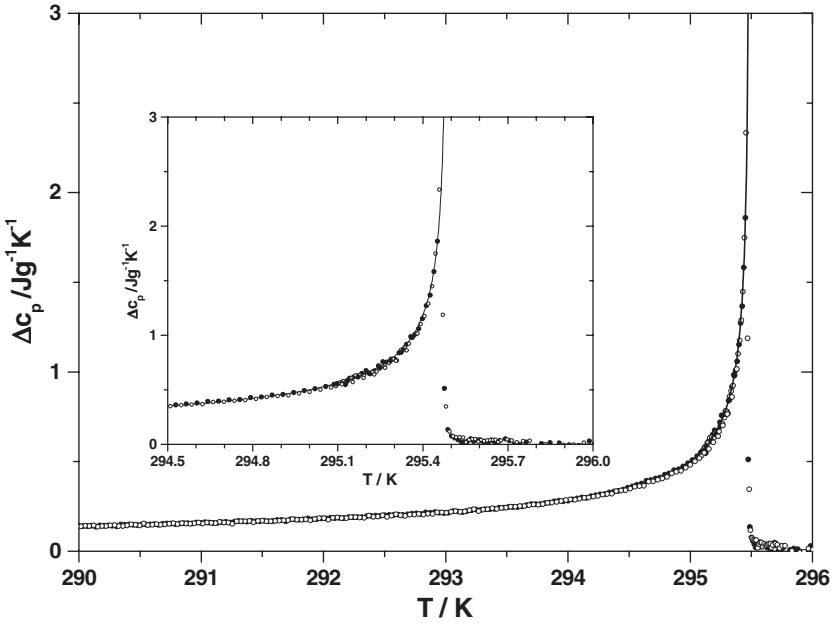

Figure 2. Specific heat excess of TGSe obtained in the dissipation branch (c_d) (open circles) and in the relaxation branch (c_r) (filled circles). The solid curve represents the best fit of experimental data to a 2–6 Landau potential.

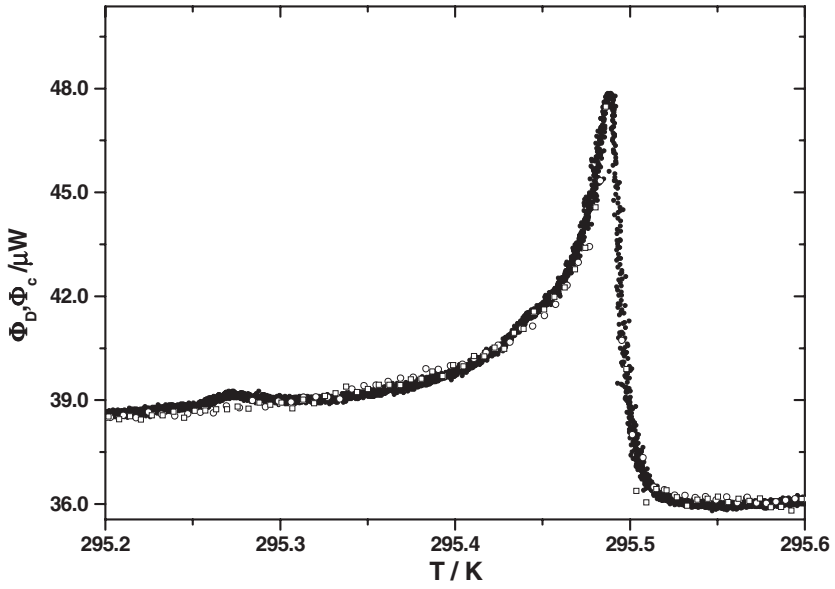

Figure 3. DTA trace (filled circles) and DTA trace calculated from specific heat data obtained on cooling (open circles) and on heating (open squares).

transition, is only about 10 μW, as can be appreciated in the scale of figure 3. As we noted above, if the transition is first order, Φ_D and Φ_c should be different. In our case, both sets of data coincide, within the experimental error, over the entire temperature interval, so that no

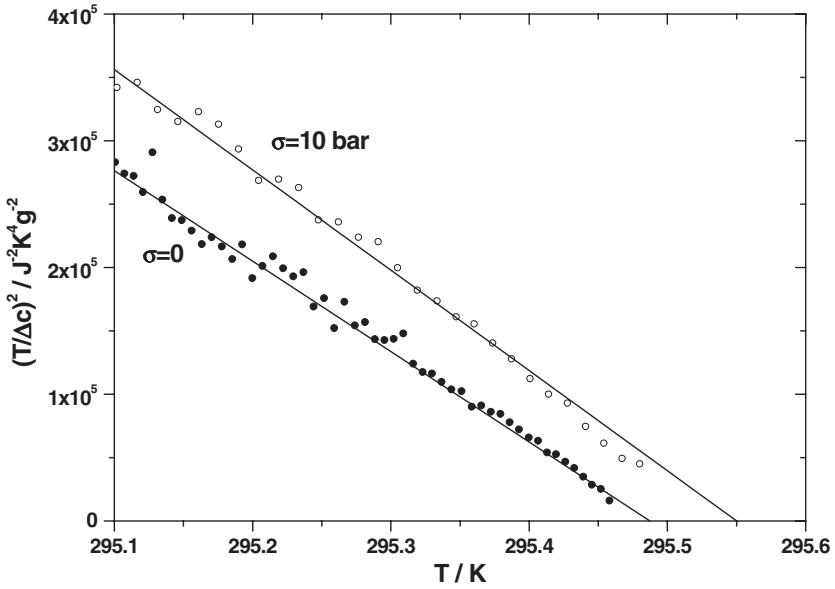

Figure 4. $(T/\Delta c_p)^2$ versus T for TGSe without stress (filled circles) and with a uniaxial stress of 10 bar along the ferroelectric axis (open circles). The best linear fit is also represented in both cases. In the graph all the specific heat data below the maximum of the specific heat are represented.

Table 1. Results of fitting the experimental data $(T/\Delta c_p)^2$ versus T and derived Landau potential coefficients.

	T_c (K)	$\frac{16C}{A^3}$ (J^{-2} K^3 g^{-2})	T_2 (K)	A (J g^{-1} K^{-1})	B (J g^{-1})	C (J g^{-1})
Cooling $\sigma = 0$	295.47	7.068×10^6	295.50	0.0818	0	24.18
Heating $\sigma = 0$	295.46	7.135×10^6	295.49	0.0814	0	24.05
Heating $\sigma = 10$ bar	295.48	7.915×10^6	295.55	0.0814	0.779	26.68

latent heat evidence was found within our experimental resolution. The important fact at this point is that the shape of the DTA trace, even at 0.2 K around the transition point, is wholly accounted for by the variation of specific heat with temperature. This result enforces the idea that the transition is continuous within our experimental resolution.

4.2. Tricritical behaviour in TGSe

To analyse the shape of specific heat it is necessary to determine the specific heat excess by subtracting the baseline. This baseline is obtained by fitting a linear temperature dependence far above T_c. This baseline is also represented in figure 1. An earlier work [11] showed that a straight line far above T_c is a very good approximation for the lattice background contribution to the specific heat. We have to keep in mind that we are interested in studying the specific heat in a small temperature range around the transition point where the specific heat excess is very great. Other choices for the baseline which were compatible with the low and high temperature data would not significantly affect the results.

In order to study this phase transition in the frame of Landau theory, we follow the previously explained procedure. As the transition is sharp, we consider the temperature of the

maximum of the specific heat as T_c. On the other hand, we represent in figure 4 $(T/\Delta c_p)^2$ versus T for the ferroelectric phase ($T < T_c$). We observe that the behaviour is practically linear. Following equation (1), we obtain from the best linear fit the slope $(16C/A^3)$ and T_2 (table 1). Since $T_2 - T_c$ is evaluated to be 0.03 K, we assume that this difference is within our experimental temperature resolution, that is, $T_c \cong T_2$, so that $B \cong 0$ and the phase transition can be considered to be just at the tricritical point. Finally, by taking $Q = 1$ at $T = 0$ K we obtain the values for A and C given in table 1.

The same procedure has been carried out for the heating curve and the results are summarized in table 1. The values for heating and cooling coincide within the experimental uncertainty.

The solid curve in figure 2 shows the 2–6 Landau prediction for the specific heat using the determined values for A, C and T_c. The inset in figure 2 shows the good agreement between the experimental data and the theoretical prediction, even very near to the transition temperature. This agreement between the experimental data and the 2–6 Landau potential justifies that $B = 0$ in our case.

We can compare this result with those obtained previously in [3]. A value of $K = 0.3 \times 10^{-3}$ was obtained, which implies $T_2 - T_c = 0.09$ K, which is bigger than the upper limit calculated in our work ($T_2 - T_c = 0.03$ K). In that case it looks reasonable to assign a value of B in the Landau potential. In this sense, our data are the nearest to the tricritical point which we have found.

Above the transition temperature the specific heat excess present a small tail, out of Landau predictions. Figure 5 shows that tail versus $T - T_c$ in a logarithmic scale to show that the tail is very similar to that obtained previously [11]. This indicates that Landau theory is verified in the ferroelectric phase, but not in the paraelectric one. The non-Landau behaviour in the paraelectric phase has been suggested before [9].

4.3. Effect of a very weak uniaxial stress

The temperature dependence of the specific heat of TGSe under a uniaxial stress of 10 bar has been measured in different runs cooling and heating the sample. The experiment has been carried out in the same conditions (heating and cooling at $v = 0.03$ K h^{-1}) and on the same previously analysed sample. We have repeated the experiments in the same conditions twice. In order to analyse Δc_p we choose the same baseline as discussed before. Figure 6 shows the Δc_p obtained for cooling and heating. In the ferroelectric phase, for $T < T_c - 0.2$ K, the specific heat excess under uniaxial stress, on cooling and heating, is lower than obtained without stress. Nevertheless, for $T_c - 0.2$ K $< T < T_c$ the specific heat on cooling and heating do not coincide. While the data on cooling experiments show a very sharp anomaly, the data on heating are slightly smeared around the transition point. Above the transition temperature, in the paraelectric phase, the tail on heating is bigger than on cooling and it is different for the two cooling experiments. We must point out that all sets of data without stress coincide.

A similar behaviour has been observed previously by Jiménez *et al* [24] in a TGS crystal doped with L-alanine (LATGS). They showed that specific heat data on cooling depend on the temperature variation rate, whereas on heating the specific heat behaviour does not depend on it. They concluded that the specific heat data on cooling do not correspond to the equilibrium. They also showed that the specific heat on cooling presents an exponential relaxation to that obtained on heating, whose time constant was approximately 14 h.

The thermodynamic effect when defects are introduced on the sample may be considered similar to an applied uniaxial stress. The relaxation time of domain growth under the influence of the stress is very high, so even in quasistatic conditions, $v = 0.03$ K h^{-1}, the specific heat

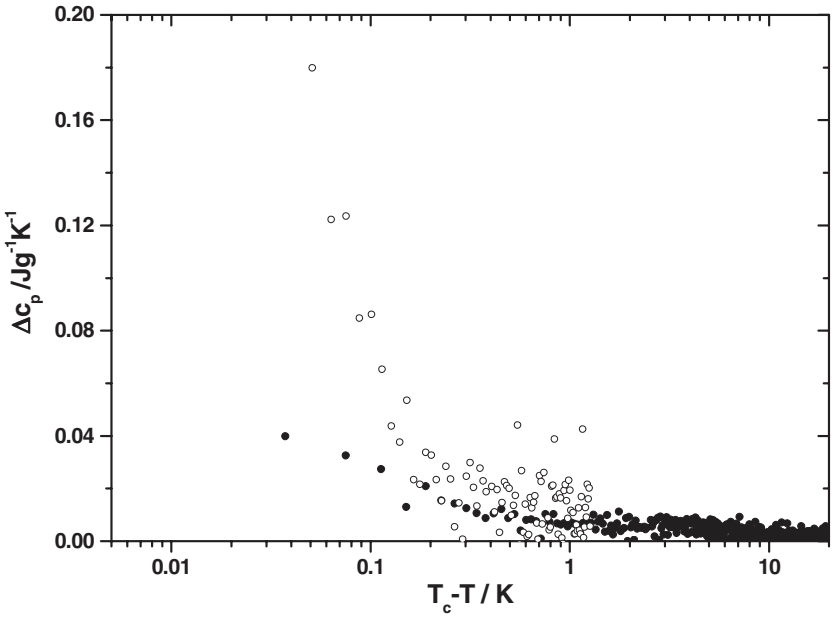

Figure 5. Specific heat excess above transition temperature versus T in a logarithmic scale, for $\sigma = 0$ (filled circles) and $\sigma = 10$ bar (open circles).

on cooling does not correspond to the equilibrium data, which should be considered those obtained on heating. We must point out that the different behaviour on cooling and heating is present only at 0.2 K below the transition temperature. Our technique provides enough experimental data in that region and has enough resolution to show the difference clearly. This effect could be masked with other techniques which have a worse temperature resolution.

According to the above discussion, we will only analyse the heating curve in the frame of Landau theory. We follow the same procedure as used for $\sigma = 0$. As the transition is sharp enough we take T_c as the maximum of specific heat. Figure 4 shows $(T/\Delta c_p)^2$ versus T for $T < T_c$ showing a linear behaviour. From the slope and the intersection with the temperature axis and taking A as the same value obtained without stress as in [3], we obtain A, B and C. All sets of data are also shown in table 1.

We observe that in this case $T_2 - T_c = 0.07$ K, that is bigger than the obtained value for $\sigma = 0$ and bigger than our experimental resolution. From this difference and using equation (2) we obtain B.

The nearness to a tricritical point is evaluated by $K = B^2/4ACT_c = (T_2 - T_c)/T_c = 0.07\ \mathrm{K}/T_c = 0.23 \times 10^{-3}$, which indicates that the transition is near to the tricritical point but now it can be considered second order.

We conclude that even the weak applied stress makes the transition clearly move away from the tricritical point. In this sense a strong coupling of the uniaxial stress with the spontaneous polarization that justifies the great effect of this weak uniaxial stress on the specific heat has been suggested previously [25].

We point out that this fact reinforces the affirmation that pure TGSe is at the tricritical point, because a small perturbation moves the system from this point. In another case a not so big effect will be produced for this very small cause.

Figure 5 also shows Δc_p versus $T - T_c$ in a logarithmic scale above the transition point. We can observe that the effect of the stress is also to produce a tail above the transition point

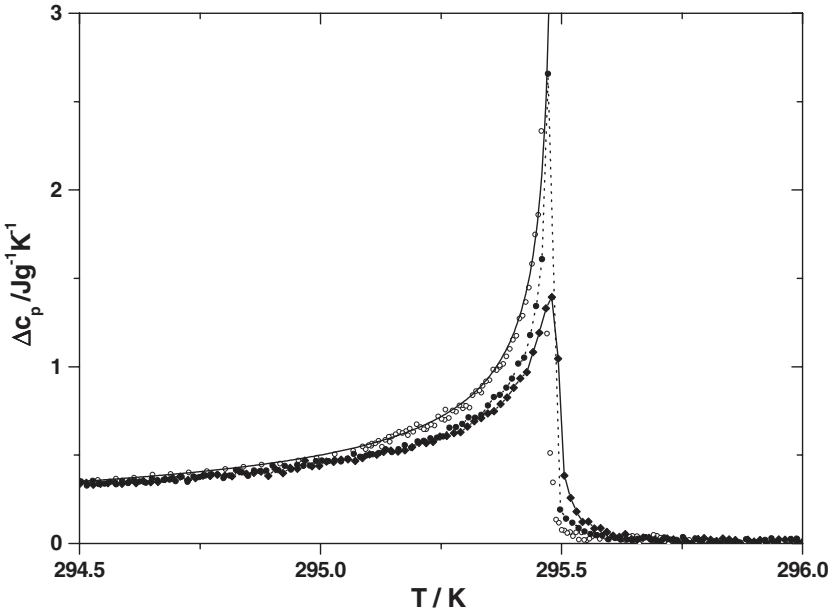

Figure 6. Specific heat excess of TGSe for $\sigma = 0$ (open circles), $\sigma = 10$ bar cooling (filled circles) and $\sigma = 10$ bar heating (filled diamonds). Curves are guides for the eyes.

much bigger than obtained without stress. This tail is bigger for heating runs than for cooling ones.

5. Conclusions

We have shown that TGSe at null stress is found to be at a tricritical point. No latent heat is found and the specific heat is fitted remarkably well by a 2–6 Landau potential whose coefficients have been determined. When a uniaxial stress of 10 bar is applied along the ferroelectric axis the transition shifts to second order.

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