

## Thermal diffusivity and critical behaviour of uniaxial ferroelectric $\text{Sn}_2\text{P}_2\text{S}_6$

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### Abstract

The anisotropy in the thermal diffusivity of uniaxial ferroelectric  $\text{Sn}_2\text{P}_2\text{S}_6$  has been measured as a function of temperature using ac photopyroelectric calorimetry. The second-order ferroelectric transition has been studied in order to ascertain the mechanisms which could explain the anomaly in specific heat through the study of the inverse of the thermal diffusivity. Landau model, as well as critical models considering the different roles of fluctuations of the order parameter and crystalline defects, are considered. Though in the ferroelectric phase the Landau model can mainly explain the anomaly in the physical properties, the fittings for the paraelectric phase show that it is necessary to take into account the influence of both fluctuations and defects to account for the results.

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### 1. Introduction

Ferroelectric phase transitions in proper uniaxial ferroelectrics  $\text{Sn}_2\text{P}_2(\text{Se}_x\text{S}_{1-x})_6$  have received considerable attention regarding their structural, dynamical and thermodynamic properties. The concentration versus temperature phase diagram [1] exhibits the Lifshitz point for  $\text{Sn}_2\text{P}_2(\text{Se}_x\text{S}_{1-x})_6$   $x=0.28$  and a virtual tricritical point at  $x=0.60$ ; these characteristics are generally thought to be the reason why the critical behaviour does not agree with the mean-field model [2].

Actually, the presence of a Lifshitz point enhances the fluctuations in the order parameter which will substantially deviate the critical exponents from the mean-field values, and this would lead to the change of the critical exponent of specific heat  $C_p$  from  $\alpha=0$  to  $\alpha=1/4$  in systems with short range interactions. On the other hand, fluctuations are strongly suppressed in ferroelectrics with strong dipolar interactions (as it is the case in this family of materials), and these are expressed as

critical exponent  $\alpha=1/6$  [3]. Another situation in which fluctuations are reduced takes place in the presence of a tricritical point; following this line, theoretical results from renormalization group analysis for uniaxial ferroelectrics in the vicinity of the tricritical Lifshitz point show that the critical exponent for specific heat must be  $\alpha=0.5$  with small logarithmic corrections [3–5].

It is important to realize that fluctuations of the order parameter are not the only justification to deviations from mean-field values in order to describe the critical behaviour of this second-order transition; these deviations can also be produced by the presence of point defects in the matrix, as has been shown in the case of structural and ferroelectric phase transitions. It has been theoretically demonstrated that point defects can contribute to the anomalies of various physical properties near ferroelectric phase transitions because they can induce long-range perturbations of the order parameter [6–8].

Critical behaviour of the ferroelectric to paraelectric transition has been previously studied for this family by means of different physical quantities: specific heat, optical birefringence, dielectric constant, ultrasonic velocity measurements [2,9–11]. The ferroelectric phase is generally well described by Landau theory but, on the other hand, it has indeed been found

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that the critical exponents which describe the critical behaviour of the ferroelectric to paraelectric transition do not fit in the framework of the mean-field approximation in the case of the paraelectric phase; besides, there is a certain level of agreement between the renormalization group analysis and some of the experimental results which has led to interpret that the vicinity of the Lifshitz point at  $x=0.28$  to the tricritical Lifshitz point on the phase diagram is the key point for that behaviour [2,11]. But still the description of the critical behaviour of these second-order phase transitions in this family is far from settled.

In this work, thermal diffusivity is measured with a high-precision technique in order to establish the validity of the different models regarding critical behaviour of  $\text{Sn}_2\text{P}_2\text{S}_6$  single crystals in the direct ferroelectric to paraelectric transition. This technique has been successfully used for the study of critical behaviour in different kind of materials with second-order phase transitions [12–14].

Single crystals cut in different orientations have been used for this study in order to check thermal anisotropy and all the samples have been used for the critical behaviour analysis. It is worth remembering that  $\text{Sn}_2\text{P}_2\text{S}_6$  has a ferroelectric monoclinic structure with point group  $m$  below 336 K, while in the paraelectric phase the point group is monoclinic  $2/m$  [15]. In the usual standard notation, the translation vectors of the monoclinic structure are  $a=9.375 \text{ \AA}$ ,  $b=7.488 \text{ \AA}$  and  $c=6.513 \text{ \AA}$  and the  $\beta$  angle between  $a$  and  $c$  is  $\beta=91.15^\circ$ . In the ferroelectric phase, the polarization vector lies in the  $a$ – $c$  plane, deviating from the  $a$ -axis by  $13^\circ$ .

## 2. Samples and experimental techniques

Single crystals of  $\text{Sn}_2\text{P}_2\text{S}_6$  were obtained by the Bridgmann method and thin slabs were cut in three orientations, with their faces perpendicular to (1 0 0), (0 1 0) and (0 0 1) directions. These samples will be called X-cut, Y-cut and Z-cut, respectively, all along the paper.

Thermal diffusivity ( $D$ ) measurements have been performed by a high-resolution ac photopyroelectric calorimeter in the standard back detection configuration [16,17]. A modulated He–Ne laser beam of 5 mW illuminates the upper surface of the sample under study. Its rear surface is in thermal contact with a  $350 \mu\text{m}$  thick  $\text{LiTaO}_3$  pyroelectric detector with Ni–Cr electrodes on both faces, by using an extremely thin layer of a high heat-conductive silicone grease (Dow Corning, 340 Heat Sink Compound). The photopyroelectric signal is processed by a lock-in amplifier in the current mode. Both sample and detector are placed inside a nitrogen bath cryostat that allows measurements in the temperature range from 77 to 500 K, at rates that vary from 100 mK/min for measurements on a wide temperature range to 10 mK/min for high-resolution runs close to the phase transitions. If the sample is opaque and thermally thick (i.e. its thickness  $\ell$  is higher than the thermal diffusion length  $\mu = \sqrt{D/\pi f}$ ,  $f$  being the modulation frequency) the natural logarithm and the phase of the normalized photopyroelectric current at a fixed temperature have a linear dependence on  $\sqrt{f}$ , with the same slope  $m$ , from which the thermal diffusivity of the sample

can be measured [16,17]:

$$D = \frac{\ell^2 \pi}{m^2} \quad (1)$$

Once the thermal diffusivity has been measured at a certain reference temperature ( $D_{\text{ref}}$ ), the temperature is changed while recording the phase of the PPE signal. Defining the phase difference as  $\Delta(T)$ , the temperature dependence of the thermal diffusivity is given by [18,19]

$$D(T) = \left[ \frac{1}{\sqrt{D_{\text{ref}}}} - \frac{\Delta(T)}{\ell \sqrt{\pi f}} \right]^{-2} \quad (2)$$

This technique is specially suited for the measurement of the through-thickness thermal diffusivity around phase transitions, since small temperature gradients in the sample produce a good signal-to-noise ratio, letting thermal diffusivity be measured with high accuracy.

Thermal diffusivity has been measured for all the samples as a function of temperature after performing an annealing at high temperature (450 K) in order to stabilize the matrix; the cooling rate was reduced as much as possible until a fixed temperature for the transition was obtained. The thicknesses of the samples were in the range 375–450  $\mu\text{m}$ . The modulation frequency chosen for the measurements was 2 Hz, after having checked that the conditions for using Eqs. (1) and (2) were fulfilled in the whole temperature range at that frequency. In particular, the linearity of the dependence of the natural logarithmic of the amplitude and phase on  $\sqrt{f}$  was well maintained in a region centered around 2 Hz. Checks at frequencies around that value gave also consistent results.

## 3. Experimental results and fitting procedures

Room temperature ( $T=300 \text{ K}$ ) thermal diffusivity measurements for the three samples give the following results:  $0.39 \text{ mm}^2/\text{s}$  for X-cut,  $0.25 \text{ mm}^2/\text{s}$  for Y-cut and  $0.33 \text{ mm}^2/\text{s}$  for Z-cut. The results for thermal diffusivity as a function of temperature for the three orientations are shown in Fig. 1; in all cases we obtain a dip at 336.0 K signalling the presence of the ferroelectric to paraelectric transition. The curves for X-cut samples and

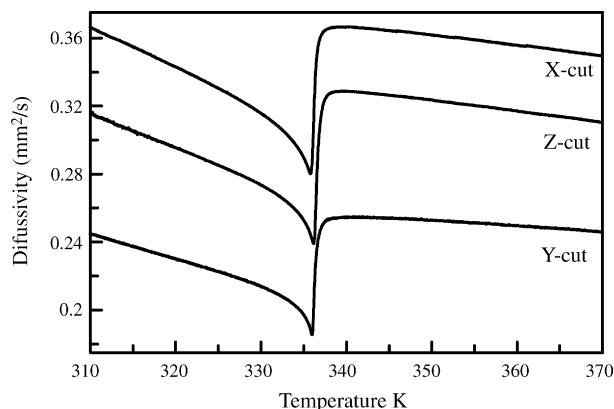


Fig. 1. Thermal diffusivity as a function of temperature for the samples cut in the three orientations.

Z-cut samples are quite similar in shape to each other, though diffusivity is a bit higher for the first orientation. For the case of Y-cut samples, the diffusivity is lower, and with a general aspect similar to the other ones, but with a certain change in the slopes. These results point to a strong thermal anisotropy, especially in the direction perpendicular to the XZ plane. There is some small rounding in the experimental curves, as usual. This rounding is inherent to the intrinsic characteristics of the samples and not to the technique, as previous results in other materials show [20]. The use of single crystals is essential in order to reduce that rounding as much as possible.

In order to study the critical behaviour of the transition, we have obtained very well defined curves over a wide temperature range. As the relation between specific heat  $C_p$  and thermal diffusivity  $D$  is:

$$D = \frac{K}{\rho C_p} \quad (3)$$

(where  $K$  is the thermal conductivity and  $\rho$  is the density of the material), the critical behaviour of specific heat and the inverse of thermal diffusivity is the same provided that neither thermal conductivity nor density have significant changes at the transition, which is the case in this material, as our own measurements and those from [21] show. Fig. 2 shows, as an example, thermal conductivity in the vicinity of the transition temperature for one of the samples, obtained from the combination of amplitude and phase of the photopyroelectric signal [16,17]; there is no singularity but a smooth decrease with temperature. The vertical axis scale has been chosen to be in an equivalent proportion to that of Fig. 1.

To start with, we approached the problem through the mean-field analysis in terms of Landau theory where we are taking into account the possible coupling of polarization to strain in a uniaxial ferroelectric and so Landau thermodynamical potential density reads:

$$F = F_0 + \frac{\alpha}{2} P^2 + \frac{\beta}{2} P^4 + \frac{\gamma}{2} P^6 + \frac{1}{2} cu^2 + ruP^2 \quad (4)$$

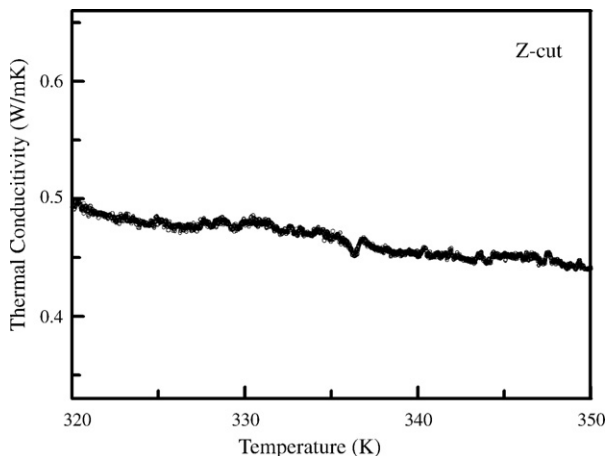


Fig. 2. Thermal conductivity for the Z-cut sample as a function of temperature in the vicinity of the transition temperature.

where  $F_0$  is the value in the paraelectric phase,  $\alpha = at$  (being  $t = T - T_0$  with  $T_0$  the transition temperature and  $a = \partial\alpha/\partial t$  is related to the Curie–Weiss constant),  $\beta$  and  $\gamma$  are phenomenological coefficients which do not depend on temperature,  $c = c_{ijkl}$  is elastic module matrix,  $u = u_{ij}$  is deformation tensor and  $r = r_{ijkl}$  is the electrostriction coefficient [22].

We follow the usual procedure of minimizing the free energy with respect to both polarization  $P$  and strain  $u$ , in order to obtain the equilibrium value of the order parameter in the ferroelectric phase, so that we can obtain for the isobaric specific heat in the ferroelectric phase:

$$C_p = -T \left( \frac{\partial^2 F}{\partial T^2} \right)_P = C_p^0 + \frac{a^2}{2\beta'} \frac{T}{\sqrt{1-4At}} \quad (5)$$

where  $C_p^0$  is the specific heat in the paraelectric phase,

$$\beta' = \beta - \frac{2r}{c^2} \quad (6a)$$

$$A = \frac{\gamma a}{\beta'^2} \quad (6b)$$

So the anomalous part of the specific heat can be expressed as

$$\Delta C_p = \frac{a^2}{2\beta'} \frac{T}{\sqrt{1-4At}} \quad (7)$$

Taking into account Eq. (3), the following relationship between the anomalous part of the specific heat and the corresponding quantity for the inverse of thermal diffusivity can be used,

$$\Delta C_p = \frac{K}{\rho} \Delta \left( \frac{1}{D} \right) \quad (8)$$

provided that neither thermal conductivity nor density have significant changes at the transition, which is the case in this material.

So the equation which will express the anomalous part of the inverse of thermal diffusivity due to the transition reads,

$$\Delta \left( \frac{1}{D} \right) = p_1 \frac{T}{\sqrt{1-4p_2(T-T_0)}} \quad (9)$$

where  $p_1$  and  $p_2$  are the adjustable parameters readily related to the different parameters in Landau expansion using Eqs. (6)–(8). In the fitting procedure, a linear background has been subtracted to the experimental curves using experimental points at temperatures high above the transition (around 370 K), where there is a linear relationship between  $1/D$  and  $T$ .

In Fig. 3 we can see the experimental results and the fittings for the three samples using Eq. (9); Table 1 contains the relevant parameters of the fitting, where the coefficient of determination  $R^2$  expresses the quality of the fitting.

In order to check the appropriateness of using the renormalization group theory to explain the critical behaviour of the ferroelectric to paraelectric transition, we have performed fittings of the paraelectric experimental curves in the near vicinity of the transition temperature using the functions which corre-

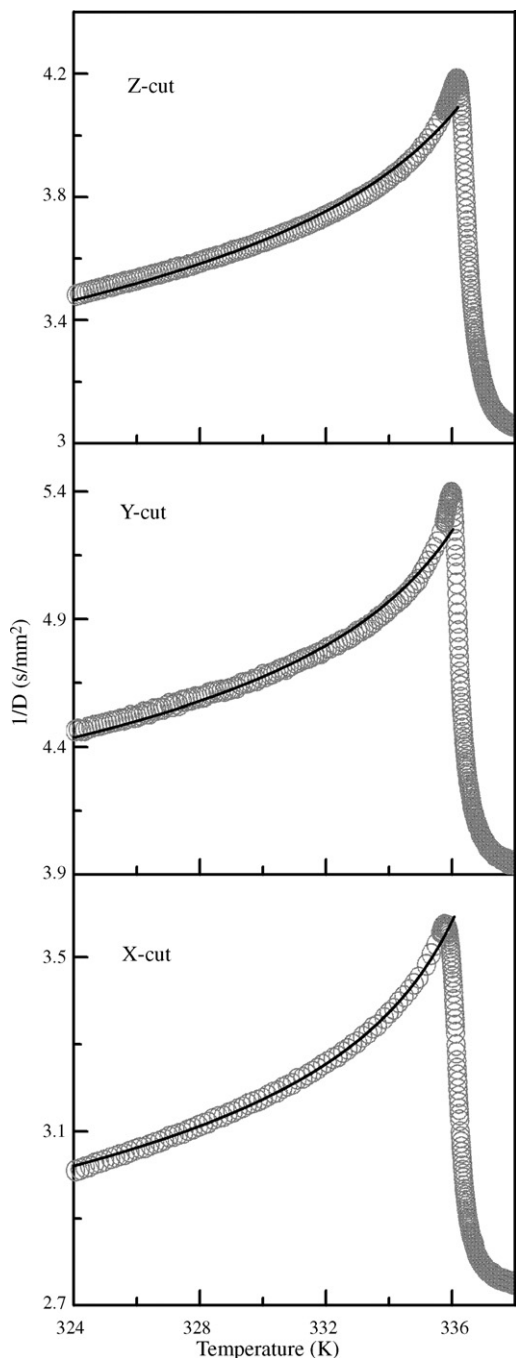


Fig. 3. Experimental (circles) and fitted (line) curves for the inverse of thermal diffusivity as a function of temperature using the Landau mean-field model (Eq. (9)) in the ferroelectric phase, for the three samples.

spond to the different models [2,4,9,10], the first one being,

$$\Delta \left( \frac{1}{D} \right) = A_1 \left( \frac{T - T_0}{T_0} \right)^{-\alpha} \quad (10)$$

where  $\alpha = 0.5$  corresponds to the square root power law theory obtained when taking into account first-order fluctuations and  $T_0$  is the critical temperature.

The second fitting expression is,

$$\Delta \left( \frac{1}{D} \right) = A_2 \left( \frac{T - T_0}{T_0} \right)^{-0.5} \left| \ln \left( \frac{T - T_0}{T_0} \right) \right|^b \quad (11)$$

where a logarithmic correction has been introduced, which considers the possibility of the attenuation of fluctuations in the order parameter; this effect would have reduced in Eq. (10) the critical value  $\alpha$  if it were present.

Lastly we have also taken into account the possible superposition of fluctuation effects and the contribution of defects [6,7].

$$\Delta \left( \frac{1}{D} \right) = A_3 \left( \frac{T - T_0}{T_0} \right)^{-0.5} + B \left( \frac{T - T_0}{T_0} \right)^{-1.5} \quad (12)$$

In the three cases a linear background has been considered and subtracted as it was done for the case of the Landau-potential fitting. The conditions of the fittings and the parameters obtained for all cases are shown in Table 2. The experimental and fitted curves for the three samples and for Eqs. (10) and (12) are shown in Figs. 4 and 5, respectively.

#### 4. Discussion

From the thermal diffusivity results obtained at room temperature, thermal conductivity values can be obtained through Eq. (3) using the specific heat data shown in [9]. So, thermal conductivity at 300 K gives the following values: 0.68 W/mK for X-cut, 0.44 W/mK for Y-cut, and 0.58 W/mK for Z-cut. These room temperature values are quite low meaning that they are not good thermal conductors and they are very similar to other found, for example, in TGS, which is another ferroelectric material with monoclinic symmetry (see Fig. 979 in [23]). There is a ratio of 1.5 between the higher and the lower values in  $\text{Sn}_2\text{P}_2\text{S}_6$  while in TGS it is about 1.3, so the anisotropy is stronger but not too different. From Fig. 1 we can see that the behaviour as a function of temperature is quite similar in each direction but heat is transferred more easily in the XZ plane (where polarization vector lies) than in the direction perpendicular to it, giving rise to thermal anisotropy. This reduction is surely due to the increment

Table 1  
Results of the fitting of the inverse of thermal diffusivity using the Landau model (Eq. (9))

	X-cut	Y-cut	Z-cut
$p_1$ (mm <sup>2</sup> /s)	2566.73 ± 1.63	4258.26 ± 7.11	3321.83 ± 4.12
$p_2$ (K <sup>-1</sup> )	0.0785 ± .0002	.0615 ± .0003	0.0512 ± 0.0002
Range adjusted	$3.2 \times 10^{-2} - 2 \times 10^{-3}$	$3.2 \times 10^{-2} - 2 \times 10^{-3}$	$3.2 \times 10^{-2} - 2 \times 10^{-3}$
$R^2$	0.99905	0.98846	0.99218

The columns show the adjustable parameters  $p_1$  and  $p_2$ , the range adjusted in reduced temperature units  $t = (T - T_0)/T_0$  and the quality of the fitting through the coefficient of determination  $R^2$ .

Table 2

Results of the fitting of the inverse of thermal diffusivity using Eqs. (10)–(12) for the three samples

		X-cut	Y-cut	Z-cut
Eq. (10)	$A_1$ (mm <sup>2</sup> /s)	$3.438 \times 10^{-5} \pm 1.0 \times 10^{-7}$	$3.913 \times 10^{-4} \pm 8.6 \times 10^{-6}$	$9 \times 10^{-5} \pm 3.2 \times 10^{-6}$
	$\alpha$	$1.355 \pm .003$	$1.047 \pm .003$	$1.278 \pm .005$
	Range adjusted	$6.8 \times 10^{-4}$ – $2.7 \times 10^{-2}$	$5 \times 10^{-4}$ – $2.7 \times 10^{-2}$	$6.8 \times 10^{-4}$ – $2.7 \times 10^{-2}$
	$R^2$	0.992	0.991	0.986
Eq. (11)	$A_2$ (mm <sup>2</sup> /s)	$2.11 \times 10^{-7} \pm 1.1 \times 10^{-9}$	$1.019 \times 10^{-5} \pm 4.3 \times 10^{-7}$	$8.42 \times 10^{-7} \pm 5.3 \times 10^{-8}$
	$\beta$	$5.69 \pm .02$	$3.80 \pm .02$	$5.18 \pm .03$
	Range adjusted	$6.8 \times 10^{-4}$ – $2.7 \times 10^{-2}$	$5 \times 10^{-4}$ – $2.7 \times 10^{-2}$	$6.8 \times 10^{-4}$ – $2.7 \times 10^{-2}$
	$R^2$	0.994	0.993	0.989
Eq. (12)	$A_3$ (mm <sup>2</sup> /s)	$1.40 \times 10^{-3} \pm 5 \times 10^{-5}$	$8.42 \times 10^{-3} \pm 6 \times 10^{-5}$	$3.25 \times 10^{-3} \pm 6 \times 10^{-5}$
	$B$ (mm <sup>2</sup> /s)	$1.148 \times 10^{-5} \pm 5 \times 10^{-8}$	$9.51 \times 10^{-6} \pm 8 \times 10^{-8}$	$1.62 \times 10^{-5} \pm 1 \times 10^{-7}$
	Range adjusted	$6.8 \times 10^{-4}$ – $2.7 \times 10^{-2}$	$5 \times 10^{-4}$ – $2.7 \times 10^{-2}$	$6.8 \times 10^{-4}$ – $2.7 \times 10^{-2}$
	$R^2$	0.990	0.983	0.981

In each case the two corresponding adjustable parameters are shown together with the range adjusted in reduced temperature units  $t = (T - T_0)/T_0$  and the quality of the fitting through the coefficient of determination  $R^2$ .

of scattering mechanisms which reduce the mean free path of phonons in (0 1 0) direction.

Concerning the critical behaviour, results shown in Fig. 3 show that the application of Landau theory fits the ferroelectric phase to some extent, though for the Z-cut sample the agreement is not so good. The observed overshoot of experimental points over calculated mean field curves near the phase transition may be determined by some contributions of order parameter fluctuations and defects. Defects are usually responsible for a rounding in the physical properties anomalies at phase transitions, but Isaverdiev et al. [8] have demonstrated that, in the case of charge defects in ferroelectrics, they can give rise to stronger anomalies. In order to check the validity of the parameters obtained in the fitting of the inverse of the thermal diffusivity, we have worked out the parameter  $\beta'$  which appears in the specific heat Eq. (7) and which contains the phenomenological Landau parameter  $\beta$  as well as the coupling parameters which are sensitive to the orientation of the sample (see Eq. (6a)).  $\beta'$  is related to the fitted parameter  $p_1$  through the expression  $p_1 = a^2/2\beta'K$  where 'a' is the phenomenological constant related to the Curie–Weiss constant in the Landau expansion and  $K$  is thermal conductivity. We have used for this calculation the 'a' value obtained by Khoma from dielectric permittivity measurements [22], and is  $a = 1.6 \times 10^6 \text{ J m K}^{-1} \text{ C}^{-2}$ . The results are  $\beta' = 8.5 \times 10^8 \text{ J m}^5 \text{ C}^{-4}$  for X-cut sample,  $\beta' = 6.4 \times 10^8 \text{ J m}^5 \text{ C}^{-4}$  for Y-cut sample and  $\beta' = 6.1 \times 10^8 \text{ J m}^5 \text{ C}^{-4}$  for Z-cut sample, so the mean value is  $7.0 \times 10^8 \text{ J m}^5 \text{ C}^{-4}$  which is quite close to previous results obtained for different authors [11,22] measuring other physical quantities. The difference in the three values for the samples in different orientations is not significant enough so as to obtain any definite conclusions about anisotropic properties. Moreover, the value of the phenomenological parameter  $\gamma$  in the Landau expansion that we can obtain from parameters  $p_2$  and  $\beta'$  through the expression  $p_2 = \gamma a/\beta'^2$  has a mean value of  $2.3 \times 10^{10} \text{ J m}^9 \text{ C}^{-6}$  which is quite close to the value of  $3.5 \times 10^{10} \text{ J m}^9 \text{ C}^{-6}$  obtained by Vysochanskii and Grabar [24].

This means that, indeed, the Landau theory is of application for the ferroelectric phase and the order of magnitude of

the results coincide quite well with previous results obtained through other physical quantities.

We turned our attention to the paraelectric phase. The fittings obtained by means of Eqs. (10)–(12) confirm that the critical behaviour does not agree with the mean-field model, because in the three cases we could obtain a good fitting with different sets of parameters which do not correspond to that model.

Starting with Eq. (10), if the first fluctuations correction (or Gaussian critical behaviour) is the main cause of that deviation, we should have obtained a good fitting with parameter  $\alpha = 0.5$ , but in Table 2 we see that the best fittings were obtained with  $\alpha = 1.35$  for X-cut,  $\alpha = 1.05$  for Y-cut and  $\alpha = 1.27$  for Z-cut, values extremely far from the theoretical value. All the fittings are of quite a good quality, what can be confirmed by the coefficient of determination  $R^2$ , which is quite close to unity. Fig. 4 shows the experimental and fitted curve in this case. In the insets of that figure,  $(1/D) - (1/D)_{\text{background}}$  is represented as a function of the reduced temperature  $t = (T - T_0)/T_0$ , in a logarithmic scale, so that we can see that, even if the fitting is good, Eq. (10) can not follow the curvature of the experimental curve.

Logarithmic corrections are meaningful when the fitted  $\alpha$  value is less than 0.5 because the fluctuations are lessened by different effects, such as strong dipole forces and being close to a tricritical point. With the high values we have obtained for  $\alpha$  it would not make any sense if we could fit the experimental curves to Eq. (11). To prove that point we have performed those fittings and the results are also presented in Table 2. We can obtain a very good fitting to Eq. (11) but with an exponent  $b$  for logarithmic correction extremely high, devoid of any physical meaning: 6.2 for X-cut, 3.81 for Y-cut, and 4.65 for Z-cut. Theoretical calculations give a range  $0.1 < b < 0.33$  if the logarithmic correction were applicable [3,4].

In the case of the fitting to Eq. (12), where the deviation from the mean-field value is accounted both by fluctuations and by the presence of defects, we achieved quite a good result and with a sound physical meaning. The experimental and fitted curves are shown in Fig. 5, where in the insets  $\log((1/D) - (1/D)_{\text{background}})$  versus  $\log((T - T_0)/T_0)$  is represented in order to follow the appropriateness of the fitting close to the critical temperature.



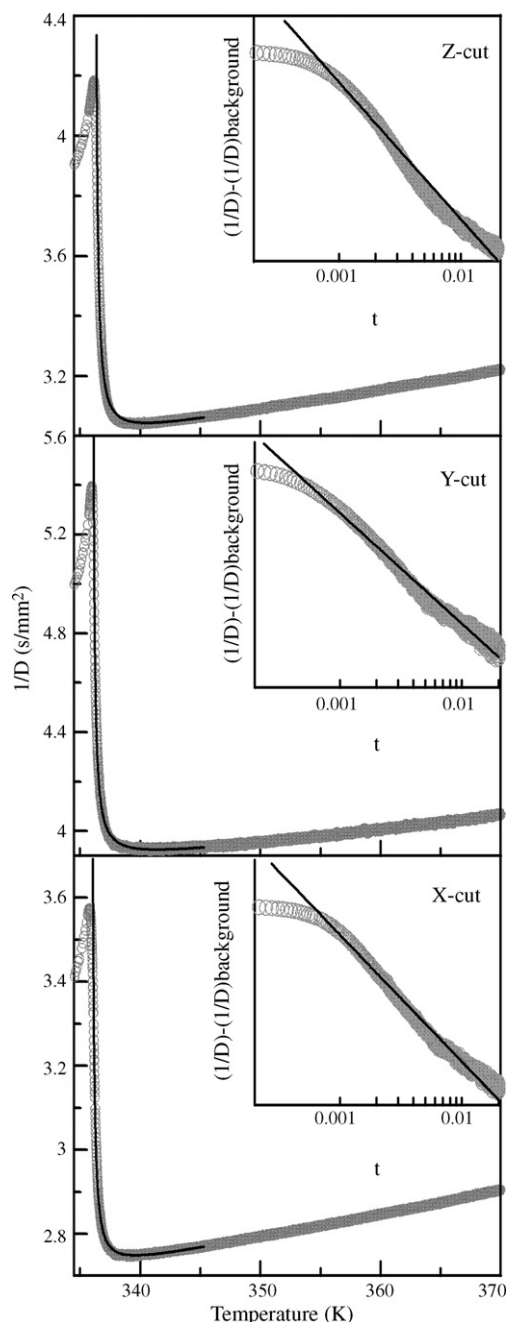


Fig. 4. Experimental (circles) and fitted (line) curves for the inverse of thermal diffusivity as a function of temperature using the first-fluctuational correction model (Eq. (10)) in the paraelectric phase. In every inset the vicinity of the transition is shown with a logarithmic plot: in the vertical axis the linear background has been subtracted to the inverse of the thermal diffusivity,  $(1/D) - (1/D)_{\text{background}}$  while in the horizontal axis  $t = (T - T_0)/T_0$ ; the circles stand for the experimental and the line for the fitted curves.

In Table 2 the coefficients  $A_3$  and  $B$  show the different contributions of fluctuations and defects. In the three cases the amplitude of the defect contribution is much less than the amplitude of the fluctuational contribution to the critical anomaly:  $B/A_3$  is equal to  $8.2 \times 10^{-3}$  for X-cut,  $1.1 \times 10^{-3}$  for Y-cut and  $5.0 \times 10^{-3}$  for Z-cut.

So the contribution of defects is dominating in the near vicinity of the critical transition, where we found that Eq. (10) did

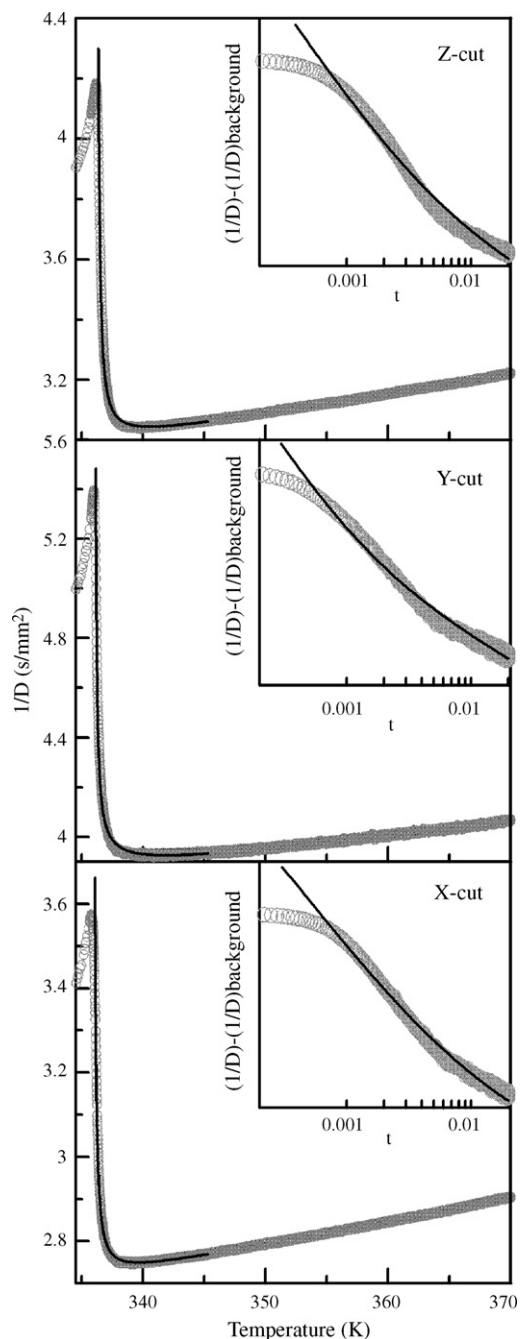


Fig. 5. Experimental (circles) and fitted (line) curves for the inverse of thermal diffusivity as a function of temperature using the model with take into accounts both fluctuations and defects (Eq. (12)) in the paraelectric phase. In every inset the vicinity of the transition is shown with a logarithmic plot: in the vertical axis the linear background has been subtracted to the inverse of the thermal diffusivity,  $(1/D) - (1/D)_{\text{background}}$  while in the horizontal axis  $t = (T - T_0)/T_0$ ; the circles stand for the experimental and the line for the fitted curves.

not hold for  $\alpha = 0.5$ . Besides, the Ginzburg criterium gives us the scale in which we can apply the first fluctuational correction for Landau theory [25]. This number in the isostructural  $\text{Sn}_2\text{P}_2\text{Se}_6$  is  $10^{-2}$  [26] which means that if the reduced temperature is higher than that value, the critical behaviour might be described by a first fluctuational correction, but not necessarily for lower values.

Up to now, the critical behaviour of uniaxial ferroelectrics  $\text{Sn}_2\text{P}_2(\text{Se}_x\text{S}_{1-x})_6$  has been explained in terms of the nearness of a Lifshitz point to the tricritical Lifshitz point, so that the enhancement of fluctuations could be reduced by the presence of the tricritical point in combination with long-range dipole-dipole interactions, and a logarithmic correction was appropriate for the description. But our results show that in real systems the influence of point defects must be considered, which complicates the observation of small logarithmic corrections. These point defects are responsible for inducing long-range perturbations of the order parameter, thus getting away from the mean-field model.

On the other hand, there is an interesting physical question still to be solved in ferroelectric transitions and it has been proved again in this case. Scaling laws should be applicable to both ferroelectric and paraelectric phases in the near vicinity of the second-order transition with the same critical exponents for both phases, which means that the same universality class should hold at both sides. In this case, the ferroelectric phase follows reasonably well the mean-field model while the paraelectric phase clearly deviates from this model and can be interpreted by means of fluctuations of the order parameter and contribution of defects. And, for this particular case of second-order phase transition near the Lifshitz point and not far from the tricritical point on a state diagram in uniaxial ferroelectrics, there is no model to tell us the relative importance of the contribution of fluctuations (and also from defects) to the ferroelectric and paraelectric phases. The consequence is that it has not been possible to obtain a proper fitting to both phases simultaneously with the same exponents and with physical meaning as it is usual in the case of magnetic transitions. More theoretical development needs still to be done to clearly describe static critical behaviour at this second-order ferroelectric transitions.

## 5. Conclusions

Thermal diffusivity as a function of temperature has been studied in single crystals of uniaxial ferroelectric  $\text{Sn}_2\text{P}_2\text{S}_6$  cut in three orientations parallel to the unit cell vectors, showing that heat transfer is easier in the XZ plane, where polarization vector lies, than in a direction perpendicular to it. Critical behaviour has been studied through the inverse of the thermal diffusivity. The fitting to the Landau model can, to a great extent, explain the ferroelectric phase and this is strongly supported by the fact that the phenomenological coefficients of that expansion obtained in this work agree with those obtained studying other physical properties. The paraelectric phase, on the other hand, does not agree with a mean field model. The critical behaviour can be well explained by a combination of fluctuations of the order parameter and the contribution of crystalline defects, being this last one especially important in the near vicinity of the ferroelectric transition.

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