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Thermal Diffusivity and Critical Behaviour of Uniaxial Ferroelectric $Pb_5Ge_3O_{11}$

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Thermal diffusivity of uniaxial ferroelectric $Pb_5Ge_3O_{11}$ 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. It has been shown that $Pb_5Ge_3O_{11}$ falls within the universality class of the mean-field model: the ferroelectric phase is very well explained within the framework of the Landau model, while in the paralectric phase a logarithmic correction must be taken into account, as predicted by renormalization group theory.

Keywords Critical phenomena; ferroelectricity; phase transition; thermal diffusivity; thermodynamic properties

1. Introduction

Lead germanate crystal $Pb_5Ge_3O_{11}$ is a uniaxial ferroelectric with interesting applications as pyroelectric material. It exhibits a second-order phase transition from the ferroelectric phase with trigonal group P3 to the paraelectric phase with a hexagonal space group $P\bar{6}$, at 450 K [1]. The structure consists of two layers arranged alternately along the c-axis in the Pb frame: a layer of GeO_4 tetrahedra and a layer of Ge_2O_7 double tetrahedra [2, 3]. Different research groups have studied the dielectric, optical, pyroelectric, elastic or electromechanical properties [4–10]. On the other hand, thermal properties (such as specific heat, thermal conductivity, thermal diffusivity), have been scarcely studied [11].

There is agreement that the second order transition in this uniaxial ferroelectric is well described by the Landau theory [12, 13], but the critical behaviour of the transition has been studied so far only through spontaneous polarization [13, 14] and susceptibility data [5, 15, 16], with no attempts to obtain it through thermal properties such as specific heat or related magnitudes. The purpose of this work is to study the critical behaviour of the ferroelectric to paraelectric transition through the study of thermal diffusivity, using a high-resolution

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photopyroelectric technique. For the ferroelectric phase, the validity of Landau theory has been tested. Concerning the paralectric phase, renormalization group theory states that the critical behaviour of the specific heat in uniaxial ferroelectrics falls within the universality class of the mean field model (critical exponent $\alpha = 0$) but with a logarithmic correction [17, 18]. This logarithmic correction, the conditions in which it can be fulfilled and possible alternative models taking into account the influence of dipolar interactions or the presence of defects on the fluctuations of the order parameter, have been discussed and compared to experimental results in other uniaxial ferroelectrics such as TGS and $Sn_2P_2S_6$ but not in this germanate [18–21].

2. Samples and Experimental Techniques

Single crystals of $Pb_5Ge_3O_{11}$ were obtained by the Czochralski method and thin slabs were cut in three orientations, with their faces perpendicular to [100], [010] and [001] directions.

Thermal diffusivity (D) measurements have been performed by a high-resolution ac photopyroelectric calorimeter in the standard back detection configuration [22, 23]. 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 μm thick $LiTaO_3$ 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 an oven that allows measurements in the temperature range from room temperature up to 600 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 ℓ 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 exhibits a linear dependence on $\sqrt{f}$, with the same slope m, from which the thermal diffusivity of the sample can be measured [22, 23]:

$$D = \frac{\ell^2 \pi}{m^2} \tag{1}$$

Once the thermal diffusivity has been measured at a certain reference temperature (D_{ref}), the temperature is changed while recording the phase of the photopyroelectric signal. Defining the phase difference as $\Delta(T)$, the temperature dependence of the thermal diffusivity is given by [24, 25]

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

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. The thicknesses of the samples were around 400 μm. The modulation frequency chosen for the measurements was 4 Hz, after having checked that the samples are thermally thick in the whole temperature range. 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 centred around 4 Hz. Checks at frequencies around that value gave the same results.

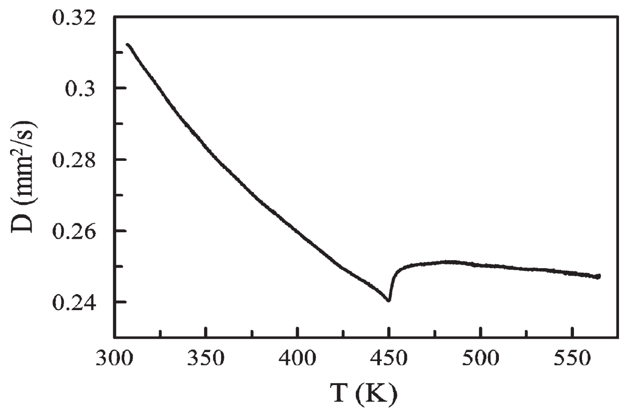

Figure 1. Thermal diffusivity as a function of temperature.

3. Experimental Results and Fitting Procedures

Room temperature (T = 300 K) thermal diffusivity measurements for the three samples gave a value of 0.31 ± 0.01 mm^2/s irrespective of the orientation. The temperature dependence of thermal diffusivity is shown in Fig. 1. The same results, within experimental accuracy, are obtained for the three orientations, indicating that there is no thermal anisotropy. A dip at 450 K indicates the presence of the ferroelectric to paraelectric phase transition. There is some 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 [26]. 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 D(T) recorded within a wide temperature range. As the relation between specific heat c_p and thermal diffusivity D is

$$D = \frac{K}{\rho c_p} \tag{3}$$

(where K is the thermal conductivity and ρ 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 valid in this type of materials [19, 27]. Figure 2 shows the evolution of the inverse of thermal diffusivity with temperature in the region close to the phase transition, the one which will be used for the fittings.

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:

$$F = F_0 + \frac{at}{2}P^2 + \frac{\beta}{4}P^4 + \frac{\gamma}{6}P^6 + \frac{1}{2}cu^2 + ruP^2 + \cdots \tag{4}$$

where F_0 is the value in the paralectric phase, P denotes the polarization vector, a is related to the Curie-Weiss constant while t = T-T_0 with T_0 the transition temperature, β and γ are phenomenological coefficients assumed not to be temperature dependent, c = c_{ijkl} is

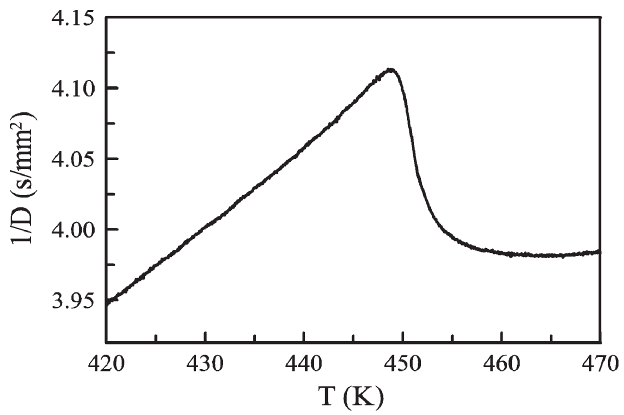

Figure 2. Inverse of thermal diffusivity as a function of temperature in the region used for the fittings to the theoretical models.

the elastic modulus matrix in the compact notation, $u = u_{ij}$ is the deformation tensor and $r = r_{ijkl}$ is the electrostriction coefficient, also in compact notations [28]; higher order terms in the expansion series are neglected.

We carried out 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 heat capacity in the ferroelectric phase

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

where C_p^0 is the heat capacity in the paraelectric phase,

$$\beta' = \beta - \frac{2r^2}{c}, \tag{6a}$$

$$A = \frac{\gamma a}{\beta'^2} \tag{6b}$$

So the anomalous part of the isobaric heat capacity can be expressed as

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

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

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

provided that neither thermal conductivity nor density have significant changes at the transition, as is the case in these ferroelectrics, as stated above.

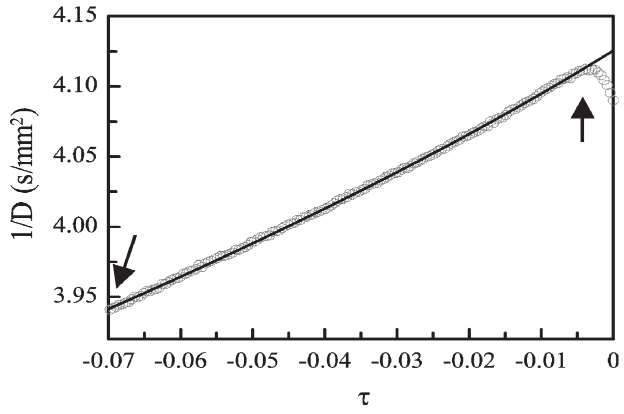

Figure 3. Experimental (circles) and fitted (line) curves for the inverse of thermal diffusivity using the Landau mean-field model (Eq. 9) in the ferroelectric phase as a function of the reduced temperature $\tau = (T - T_0)/T_0$ (not all experiemental points are shown, for the sake of clarity). The arrows indicate the fitting range: $7.0 \times 10^{-2} - 4.0 \times 10^{-3}$.

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

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

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 also been considered in order to take into account the lattice contribution to the specific heat anomaly at these temperatures, as it is customary [18, 19, 21].

In Fig. 3 we can see the experimental result and the fitting using Eq. (9), represented as a function of the reduced temperature $\tau = (T{-}T_0/T_0)$; the parameters corresponding to the best fit are $p_1 = (713.74 \pm 0.14)$ s/Km^2 and $p_2 = 0.005201(9) \times 10^{-6}$ K^{-1}; the quality of the fitting is given by the coefficient of determination $R^2 = 0.99844$. The range adjusted in reduced temperature has been $7.0 \times 10^{-2} - 4.0 \times 10^{-3}$.

Concerning the paraelectric phase, renormalization group theory states, for the case of uniaxial ferroelectrics, that critical behaviour of specific heat must correspond to a mean field model (critical exponent $\alpha = 0$) with a logarithmic correction [17, 18] so that the anomalous part of specific heat reads

$$\Delta\left(c_p\right) = A \ln\left(\frac{T - T_0}{T_0}\right) \tag{10}$$

so, after Eq. (8), the following relation should hold for the inverse of the thermal diffusivity

$$\Delta\left(\frac{1}{D}\right) = A_1 \ln\left(\frac{T - T_0}{T_0}\right) \tag{11}$$

with A_1 being the adjustable parameter.

In order to check the validity of renormalization group theory in $Pb_5Ge_3O_{11}$ 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

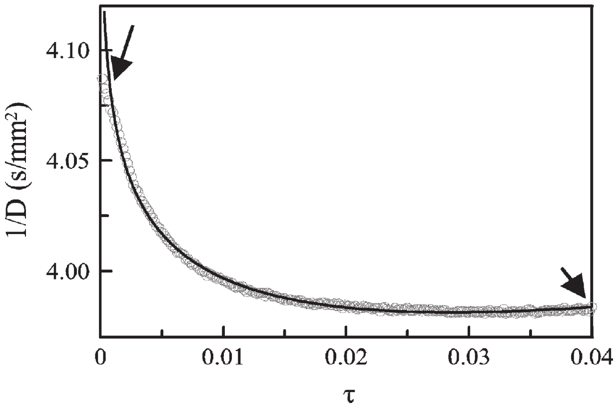

Figure 4. Experimental (circles) and fitted (line) curves for the inverse of thermal diffusivity using the logarithmic correction model (Eq. 10) in the paraelectric phase as a function of the reduced temperature $\tau = (T - T_0)/T_0$ (not all experimental points are shown, for the sake of clarity). The arrows indicate the fitting range: $4.0 \times 10^{-2} - 6.7 \times 10^{-4}$.

using Eq. (11), adding to it a linear term in reduced temperature in order to take into account the linear background, as it was done for the case of the Landau-potential fitting; this linear background accounts for the lattice contribution to the specific heat. The experimental and fitted curves are shown in Fig. 4, as a function of the reduced temperature τ in the range $4.0 \times 10^{-2} - 6.7 \times 10^{-4}$, with a coefficient of determination $R^2 = 0.99544$. The best fit corresponds to a value $A_1 = 0.038 \pm 0.001$ s/mm^2.

4. Discussion

From the thermal diffusivity result of $D_{RT} = 0.31$ mm^2/s obtained at room temperature, thermal conductivity values can be obtained through equation (3) using the specific heat data referred in literature [11]. Hence, thermal conductivity at 300 K is 0.75 W/mK, irrespective of the crystallographic direction. These room temperature values are quite low indicating that $Pb_5Ge_3O_{11}$ is a poor thermal conductor; the results are very similar to other found, for example, in TGS or $Sn_2P_2S_6$ [19], though in these last two materials there was a small but significant anisotropy in thermal conduction. On the contrary, no anisotropy has been found in this case in $Pb_5Ge_3O_{11}$, though there is anisotropy in several other physical properties such as dielectric constant or refraction index [4, 5]. As in these insulators phonons are responsible for heat transfer, there is no direct relation between the anisotropy in electrical properties and the possible anisotropy in thermal ones. Besides, general knowledge tells that thermal anisotropy in insulators is generally very weak, in spite of the presence of anisotropy in some other physical properties, as happens in this material. On the other hand, the behaviour of thermal diffusivity as a function of temperature follows the typical pattern in insulators in which there is a regular decrease from room temperature in the ferroelectric phase up to the transition temperature (where the dip signals the critical temperature) and, in the paraelectric phase, there is a change in the slope, with a softer decrease. Phonons mean free path is reduced as temperature is increased due to phonon-phonon scattering processes, aproaching a constant value because of saturation at high temperatures.

Concerning the critical behaviour, the fitting results for the ferroelectric phase shown in Fig. 3 show that the application of Landau theory fits quit well the ferroelectric phase.

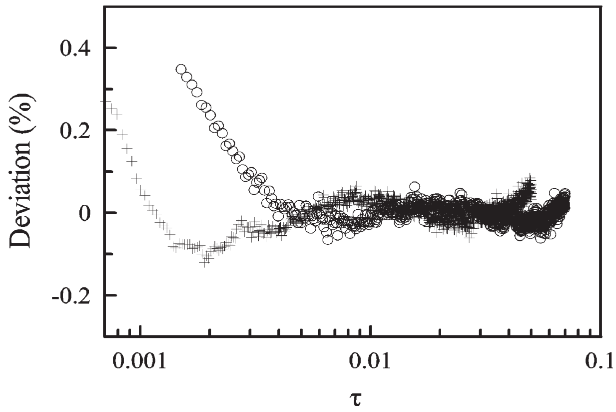

Figure 5. Deviation plot corresponding to the fittings in Figs. 3 and 4. Open circles are for $T < T_0$ and crosses for $T > T_0$.

Figure 5 shows the deviation plot, i.e. the difference between the fitted values and the measured ones, where we can clearly see the quality of the fitting performed, since the deviation ocurred lower than 0.4%. This confirms the results obtained by other authors measuring other physical quantities [12, 13]. 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 β' which appears in the specific heat Eq. (7) and which contains the phenomenological Landau parameter β as well as the coupling parameters. β' is related to the fitted parameter p_1 through the expression $p_1 = \frac{a^2}{2\beta' K}$ where 'a' is the phenomenological constant related to the Curie-Weiss constant in the Landau expansion and K is thermal conductivity. With the Curie-Weiss constant given in [5] we obtain $a = 9.67 \times 10^6$ $JmK^{-1}C^{-2}$ and consecutively $\beta' = 9.4 \times 10^{10}$ Jm^5C^{-4}. Iwasaki received a value of $\beta = 2.98 \times 10^{11}$ Jm^5C^{-4}, from the measurement of spontaneous polarization in the vicinity of the critical temperature [13]. Our β' value, though of the same order of magnitude, is lower, which might indicate that the coupling of polarization to strain needs to be taken into account for a better description and understanding of the transition mechanism. It is also of the same order of magnitude than those evaluated for TGS [29].

Furthermore, the value of the phenomenological parameter γ in the Landau expansion that we can obtain from parameters p_2 and β' through the expression $p_2 = \frac{\gamma a}{\beta'^2}$ has the value of 4.7×10^{12} Jm^9C^{-6}. As far as we know, this is the first time that this phenomenological parameter has been evaluated for $Pb_5Ge_3O_{11}$. It is a strong value compared, for instance, to the one obtained for $Sn_2P_2S_6$ [19], which indicates that this term is also important in the Landau expansion series.

In the case of the paraelectric phase, the deviation plot in Fig. 5 shows the quality of the fitting obtained by means of Eq. (10), with a deviation less than 0.3%, which confirms that the critical behaviour agrees with a mean-field model with a logarithmic correction, as renormalization group theory predicts for uniaxial ferroelectrics, reflecting the fluctuations of the order parameter in the close vicinity of the transition temperature.

5. Conclusions

Thermal diffusivity as a function of temperature has been studied in single crystals of uniaxial ferrolectric $Pb_5Ge_3O_{11}$, showing that there is no anisotropy in heat transfer. Critical behaviour has been studied through the analysis of the inverse of the thermal diffusivity. The fitting to the Landau model explains satisfactorily the ferroelectric phase and this is strongly supported by the fact that the phenomenological coefficients of that expansion obtained in this work are close to those referred in literature and obtained studying other physical properties. In the case of the paraelectric phase, the critical behaviour can be well described by the logarithmic correction to the mean field model predicted by renormalization group theory for uniaxial ferroelectrics.

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