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Critical behavior near the Lifshitz point in $\text{Sn}_2\text{P}_2(\text{S}_{1-x}\text{Se}_x)_6$ ferroelectric semiconductors from thermal diffusivity measurements

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Abstract

The thermal diffusivity of the ferroelectric family $\text{Sn}_2\text{P}_2(\text{Se}_x\text{S}_{1-x})_6$ ($0 \leq x \leq 1$) has been measured by a high-resolution ac photopyroelectric technique, using single crystals, with the aim of studying the evolution of the ferroelectric transition with Se doping. Its change from second order character to first order while passing the Lifshitz point ($x \approx 0.28$) has been evaluated, as well as the splitting of the transition at high Se concentrations. The critical behavior of the ferroelectric transition in terms of the different universality classes and their underlying physical dominant effects (tricriticality, long-range dipole interactions, Lifshitz point) has been discussed using thermal diffusivity measurements in the very close vicinity of the critical temperature. This study reveals that for Se concentrations around the Lifshitz point, long-range dipole interactions do not play a significant role and that the critical parameters are close to those predicted for the Lifshitz universality class.

1. Introduction

$\text{Sn}_2\text{P}_2(\text{S}_{1-x}\text{Se}_x)_6$ wide-gap semiconductors are attracting a renewed interest due to their photorefractive, acousto-optics, and electro-optics properties, with the result that many papers have been published in the last few years regarding their complete characterization, see [1–3] and references therein. The phase diagram [4] is particularly interesting due to the presence of a Lifshitz point at $x \approx 0.28$. This Lifshitz point separates two regions: for $x < 0.28$ there is a direct second order phase transition from the paraelectric (point group $2/m$) to the ferroelectric phase (point group m); and for $x > 0.28$ there is a second order phase transition from the paraelectric phase to an incommensurate one at T_i and then a first order phase transition from the incommensurate phase to the ferroelectric phase at T_C . In fact, this is one of the few systems in which the presence of a Lifshitz point has been experimentally confirmed. Additionally, the system

presents a tricritical point near the Lifshitz point which has been studied by simultaneously varying temperature, pressure and composition [5].

Different articles have been devoted to the study of the critical behavior of $\text{Sn}_2\text{P}_2(\text{S}_{1-x}\text{Se}_x)_6$, especially for $x = 0$ and in the vicinity of the Lifshitz point, through the study of several physical properties [6–11], but the results on the universality class they belong to are not conclusive. Therefore there is a need to obtain results with a better resolution in order to address the matter. Unlike in other ferroelectric materials, the phenomenological Landau model is shown to be inadequate to describe the properties observed at the critical temperature and so renormalization group theories have been developed for and applied to this material.

According to the critical theory, all critical behaviors can be grouped in a few universality classes characterized by the associated values of the critical exponents in the expressions of specific heat (α), magnetization (β), and susceptibility

(γ), which have been evaluated by renormalization group theories over the last 40 years. A complete revision of the universality classes related to multicritical behavior in ferroelectrics has been written by Folk [12]. Universality classes that are especially relevant to uniaxial ferroelectrics like $\text{Sn}_2\text{P}_2(\text{S}_{1-x}\text{Se}_x)_6$ are the following: L for a Lifshitz point ($\alpha = 1/4$, $\beta = 1/4$, $\gamma = 5/4$), U for a uniaxial dipole system ($\alpha = 0$, $\beta = 1/2$, $\gamma = 1$, with small multiplicative logarithmic corrections), UL for a uniaxial dipole Lifshitz system ($\alpha = 1/6$, $\beta = 1/3$, $\gamma = 7/6$), and UTL for a uniaxial dipole, tricritical, Lifshitz system ($\alpha = 1/2$, $\beta = 1/4$, $\gamma = 1$, with small logarithmic corrections). The most sensitive of these critical exponents is the one associated with specific heat, since the differences in the values are more marked from one model to another compared to β or γ .

The crux of the matter is that there is a competition among the interactions, giving rise to a variety of crossover phenomena, due to the richness of the phase diagram of $\text{Sn}_2\text{P}_2(\text{S}_{1-x}\text{Se}_x)_6$. On the one hand, the presence of a Lifshitz point enhances the fluctuations in the order parameter deviating the critical exponents from the typical mean-field values ($\alpha = 0$) to $\alpha = 1/4$ in systems with short-range interactions (L). But on the other hand, fluctuations are strongly suppressed in ferroelectrics with strong dipolar interactions leading to $\alpha = 1/6$ (UL). Finally, the presence of a tricritical point also reduces the interaction between fluctuations: in the particular case of uniaxial ferroelectrics in the vicinity of the tricritical Lifshitz point (UTL), theory predicts $\alpha = 1/2$ with small logarithmic corrections. As these critical exponents in renormalization group theory have been obtained in first loop order theory, new efforts in the last few years have been made in order to solve the problem exactly or increase it to higher accuracy. In particular, renormalization group analysis up to second order performed by Diehl gave a series of critical exponents for the Lifshitz class in agreement with previous results by Mo in which a value of about 0.2 was obtained for specific heat using a high temperature series analysis [13, 14], thus reducing the value of 0.25 obtained with first loop theory.

It is worth mentioning that in the specific heat not only the critical exponent is a characteristic value discerning the universality class, but the ratio of the amplitudes A^+/A^- as well. Although it is mathematically very difficult to predict this amplitude ratio within the framework of the renormalization group theory, it has been shown that, for the L class in the first order approximation, this amplitude is 0.30 and rises up to 0.35 in the second order approximation [15]. On the other hand, in the Gaussian approximation, at a Lifshitz point with long-range interactions this value is 0.25, while if they are neglected, it is increased to 0.42 [16].

In this work, we study the evolution of the critical behavior of $\text{Sn}_2\text{P}_2(\text{S}_{1-x}\text{Se}_x)_6$ single crystals through high-resolution thermal diffusivity measurements with an ac photopyroelectric calorimeter in order to establish the validity of the different universality classes (and so the relevance of a particular interaction) in the ferroelectric transition, for concentrations approaching and close to the Lifshitz point. Photopyroelectric techniques in general and thermal diffusivity in particular have been previously used to study phase transitions in different

kinds of solids [17–21]: the first order character can be established through a careful study of the hysteresis and the critical behavior in second order phase transitions can be studied by precisely outlining the transition in the close vicinity of the critical temperature. In this work, special attention is also paid to (a) the detection of the change of the character of the transition from second order to first order when crossing the Lifshitz point and (b) to observing the splitting of the transition in two (one second order, another first order) beyond the Lifshitz concentration, with the appearance of the intermediate phase which is well established to be incommensurate at high concentrations [22].

2. Samples and experimental techniques

Single crystals of $\text{Sn}_2\text{P}_2(\text{S}_{1-x}\text{Se}_x)_6$ were obtained by the vapor-transport method, with $x = 0, 0.15, 0.20, 0.22, 0.26, 0.28, 0.30, 0.40, 0.60, 0.80$, and 1.0. Thin slabs with their faces in monoclinic symmetry plane perpendicular to the (010) direction were cut for thermal diffusivity (D) measurements. These were performed by a high-resolution ac photopyroelectric calorimeter in the standard back detection configuration [23, 24]. A modulated He–Ne laser beam of 5 mW illuminated the upper surface of the sample. Its rear surface was in thermal contact with a 350 μm thick LiTaO_3 pyroelectric detector with metallic electrodes on both faces, by using an extremely thin layer of heat-conductive silicone grease. The area of the detector was bigger than that of the sample so that it integrated the signal coming from the heated part, assuring the equivalence with a one-dimensional (1D) illumination model. The photopyroelectric signal was processed by a lock-in amplifier in the current mode. Both sample and detector were placed inside a nitrogen bath cryostat that allowed measurements in the temperature range from 77 to 400 K, at heating/cooling rates that varied from 100 mK min^{-1} for measurements on a wide temperature range to 2 mK min^{-1} for high-resolution runs close to the phase transitions to study their critical behavior. The laser intensity was reduced down to less than 1 mW cm^{-2} , so that the temperature oscillations induced in the sample were of the order of 1 mK, while the dc contribution was about 2 mK. The sample was contained in a cryostat with nitrogen gas as exchange medium, so it was well thermalized under these conditions and the small difference between the sample holder and the sample due to the periodic heating could be safely neglected.

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 of the amplitude 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 [24, 25]:

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

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

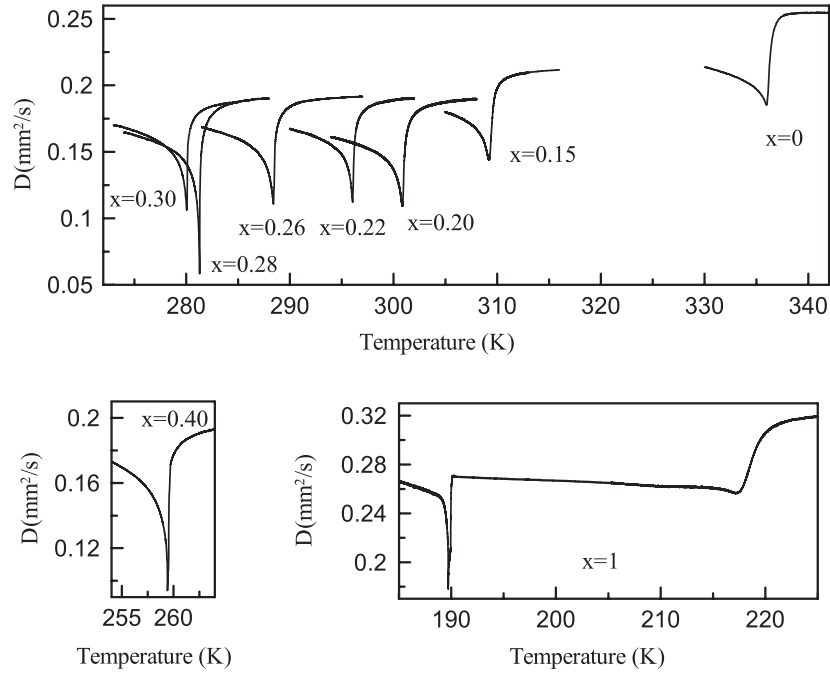


Figure 1. Thermal diffusivity as a function of temperature for the family $\text{Sn}_2\text{P}_2(\text{S}_{1-x}\text{Se}_x)_6$.

signal. Defining the phase difference as $\Delta(T)$, the temperature dependence of the thermal diffusivity is given by [26]

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

This technique is especially 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.

With this technique, thermal diffusivity along the (010) direction has been measured for all the crystals as a function of temperature. The thicknesses of the samples were in the range 400–600 μm , and the modulation frequency was in the range 0.5–2.0 Hz, depending on the sample thickness. These frequencies are high enough to fulfil the thermally thick condition but low enough to assure a high signal-to-noise ratio. Besides, heat losses by convection and radiation are negligible in this range, as they are relevant only for $f < 0.1$ Hz.

In order to study the critical behavior of the transition, we have obtained very well defined thermal diffusivity curves in the near vicinity of the critical temperatures. As thermal diffusivity is inversely proportional to specific heat c_p ($D = K/(\rho c_p)$, where K is the thermal conductivity and ρ the density), the critical behavior 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 [27, 28].

3. Experimental results and fitting procedures

3.1. Thermal diffusivity

Figure 1 shows thermal diffusivity for the samples in the vicinity of their phase transitions. For all samples, the dips in

thermal diffusivity indicate the transition from the paraelectric phase to the ferroelectric one. Starting from $x = 0$, there is a broad dip which sharpens and gets deeper as Se concentration is increased. The deepest one corresponds to the Lifshitz concentration $x = 0.28$. In the upper plot, i.e. up to $x = 0.30$, the thermal diffusivity curves are continuous, with no abrupt changes, showing the characteristic shapes of second order phase transitions. However, at $x = 0.40$, the features change: the dip is very narrow and close to T_C there are sudden changes in the diffusivity curve (see figure 3) which recall first order transitions in other materials [29]. The transition in the sample with $x = 1.0$ keeps these last features, but in this case a second step-like anomaly, at a lower temperature, takes place. At intermediate concentrations ($x = 0.6, 0.8$) there is a dip with a complex structure pointing to the splitting of the transition but the features are not well defined (the quality of the samples is worse than the rest), preventing them from being included in the figures.

Even if it is not noticeable in the scale used in figure 1, there is some small rounding at T_C . This rounding is inherent to the intrinsic characteristics of the samples and not to the technique, as previous results in other materials show [30]. In this way, the use of single crystals is essential in order to reduce that rounding as much as possible.

3.2. Hysteresis

We have studied the presence of hysteresis in the transitions for the samples in the range $0.15 \leq x \leq 0.40$ in order to check the possible evolution in the nature of the transition from second order to first order as Se is introduced in the sample. Figure 2 shows the separation in T_C between heating and cooling runs (ΔT_C) as a function of the heating rates used for the measurements. Dots represent the experimental data

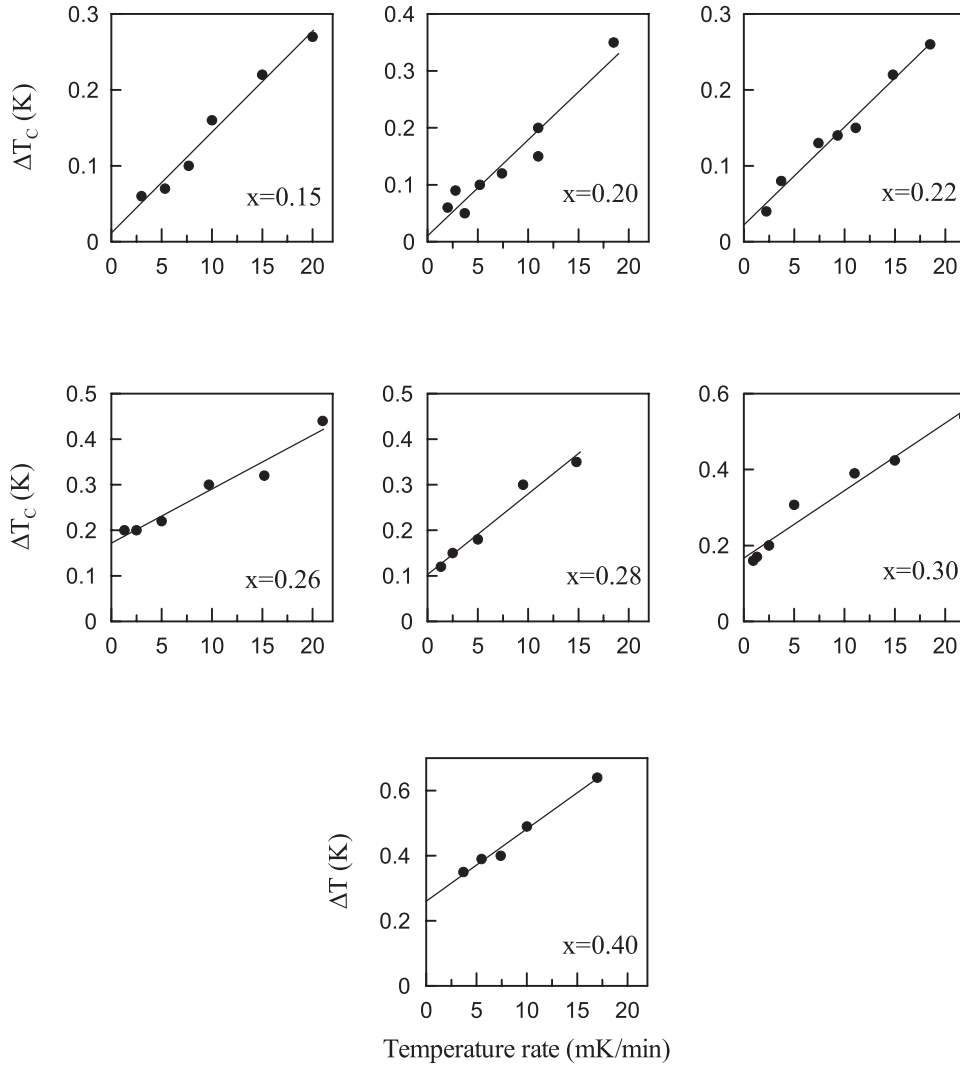


Figure 2. Experimental data (dots) and fitted lines for the thermal hysteresis ΔT_C of the ferroelectric transition for selected members of the family $\text{Sn}_2\text{P}_2(\text{S}_{1-x}\text{Se}_x)_6$.

while the continuous lines represent the linear fitting of the data, indicating the asymptotic behavior. Figure 3 plots the shapes of the thermal diffusivity curves in heating (right curve in each case) and cooling (left one) runs for some selected concentrations. This figure is introduced to appreciate the possible difference in shape between heating and cooling runs.

For $x = 0.15, 0.20,$ and 0.22 the value of ΔT_C tends to zero. Besides, the shapes of the thermal diffusivity curves in the heating and cooling runs become practically the same for small heating and cooling rates, thus supporting the absence of hysteresis. In the case of $x = 0.40$, ΔT_C tends to 0.26 K, and the shapes of the D curves in heating and cooling runs are markedly different, indicating a clear hysteresis. These features (ΔT_C tending to 0.40 K, not shown in the figure, and asymmetry in the curves on heating and cooling runs) are also present in the case of the low temperature transition for $\text{Sn}_2\text{P}_2\text{Se}_6$ ($x = 1$). For the samples with Se concentrations around the Lifshitz point ($x = 0.26, 0.28,$ and 0.30), the asymptotic tendency is to have a small remnant ΔT_C (between 0.1 and 0.2 K) together with a clear difference in the deepness

of the dip between heating and cooling runs. Accordingly a small hysteresis is confirmed.

3.3. Critical behavior

In order to study the critical behavior, the inverse of thermal diffusivity has been fitted to the customary expression used for specific heat. As explained in the previous section both magnitudes have the same critical behavior with the same critical exponent α and amplitude ratio A^+/A^- . The expression used for the fittings is

$$1/D = B + Ct + A^\pm |t|^{-\alpha} \quad (3)$$

where $t = (T - T_C)/T_C$ is the reduced temperature. Superscripts + and - stand for $T > T_C$ and $T < T_C$, respectively. The linear term represents the regular contribution to the inverse of the thermal diffusivity, while the last term represents the anomalous contribution at the second order phase transition. Scaling laws require that there is a unique critical exponent α for both branches and rigorous application

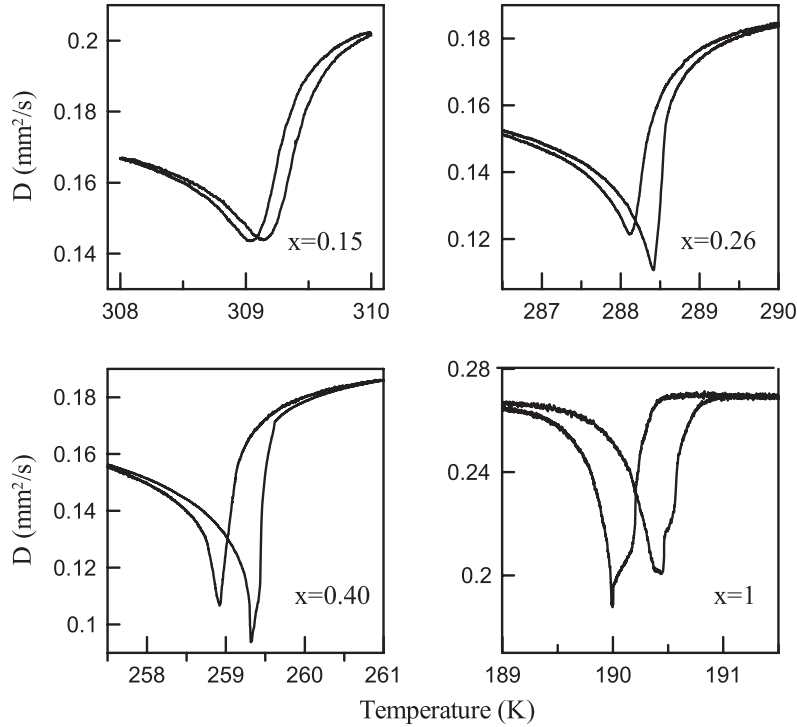


Figure 3. Details of the thermal diffusivity curves in heating (right curve in each case) and cooling (left curves) runs for $x = 0.15$ (rate 7.7 mK min^{-1}), $x = 0.26$ (rate 9.7 mK min^{-1}), $x = 0.4$ (rate 7.4 mK min^{-1}), and $x = 1$ (rate 8.0 mK min^{-1}).

Table 1. Results of the fitting of $1/D$ using equation (3). For each concentration, the critical exponent α , amplitude ratio A^+/A^- , and the critical temperature T_C are shown together with the range adjusted in reduced temperature units $t = (T - T_C)/T_C$. The coefficient R^2 measures the quality of the fitting.

| x | α | A^+/A^- | T_C (K) | Range adjusted $T < T_C$ | Range adjusted $T > T_C$ | R^2 |
|------|----------|-----------|-----------|---|---|--------|
| 0.20 | 0.14 | 0.66 | 300.93 | 8.3×10^{-3} – 3.1×10^{-4} | 3.0×10^{-5} – 7.6×10^{-3} | 0.9958 |
| 0.22 | 0.27 | 0.49 | 296.10 | 8.0×10^{-3} – 2.3×10^{-4} | 4.3×10^{-5} – 7.5×10^{-3} | 0.9980 |
| 0.26 | 0.24 | 0.48 | 288.47 | 7.9×10^{-3} – 2.9×10^{-4} | 3.3×10^{-5} – 9.1×10^{-3} | 0.9980 |
| 0.28 | 0.34 | 0.42 | 281.31 | 7.9×10^{-3} – 4.9×10^{-5} | 1.3×10^{-5} – 7.9×10^{-3} | 0.9989 |
| 0.30 | 0.21 | 0.51 | 280.05 | 8.3×10^{-3} – 1.6×10^{-4} | 1.2×10^{-5} – 8.8×10^{-3} | 0.9989 |

states that constant B needs also to be the same [31]. These conditions have sometimes been relaxed in the literature due to the difficulty of obtaining good fittings to the experimental data with that constraint, but this only makes the interpretation of results even more complicated.

At every concentration, the data were simultaneously fitted for $T < T_C$ and $T > T_C$ with a nonlinear least squares routine. First of all, we selected a fitting range close to the peak while avoiding the rounding, and kept fixed the value of T_C . Afterward, we tried to increase the number of points included in the fitting, first fixing t_{\min} and increasing t_{\max} , and then fixing t_{\max} and decreasing t_{\min} . As a last checking, we let T_C be a free parameter in order to confirm the fitting. In the whole process, we focused our attention on the root mean square (rms) deviations as well as on the deviation plots, which are the plots of the difference between the fitted values and the measured ones as a function of the reduced temperature. For this work, we have analyzed concentrations $x = 0.15, 0.20, 0.22, 0.26, 0.28,$ and 0.30 . In figure 4, the experimental data are represented by points and the continuous lines represent the best fittings to equation (3). The values of the fitting parameters

are given in table 1, while figure 5 shows the deviation plots for the range of reduced temperatures used in the fittings.

We have shown in a previous work that thermal diffusivity experimental curves for $x = 0$ could not be fitted to equation (3) using the rigorous constraints we are applying now [28]. The same stands for $x = 0.15$, and therefore it is included neither in the figures nor in the table. For $x = 0.20$, the fit is poor as can be evaluated by the R^2 value in table 1. For $x = 0.22, 0.26, 0.28,$ and 0.30 we obtain quite good fittings, with values of the critical exponent α in the range 0.24–0.34 and amplitude ratio A^+/A^- in the range 0.42–0.51.

4. Discussion

The thermal diffusivity values of the family $\text{Sn}_2\text{P}_2(\text{S}_{1-x}\text{Se}_x)_6$ are quite low meaning that these semiconductors are poor thermal conductors. The values are very similar to those found in other uniaxial ferroelectrics such as, for example, TGS [32] and $\text{Pb}_5\text{Ge}_3\text{O}_{11}$ [33]. The parent compounds ($x = 0$ and 1) show the highest thermal diffusivity. When Se and S are

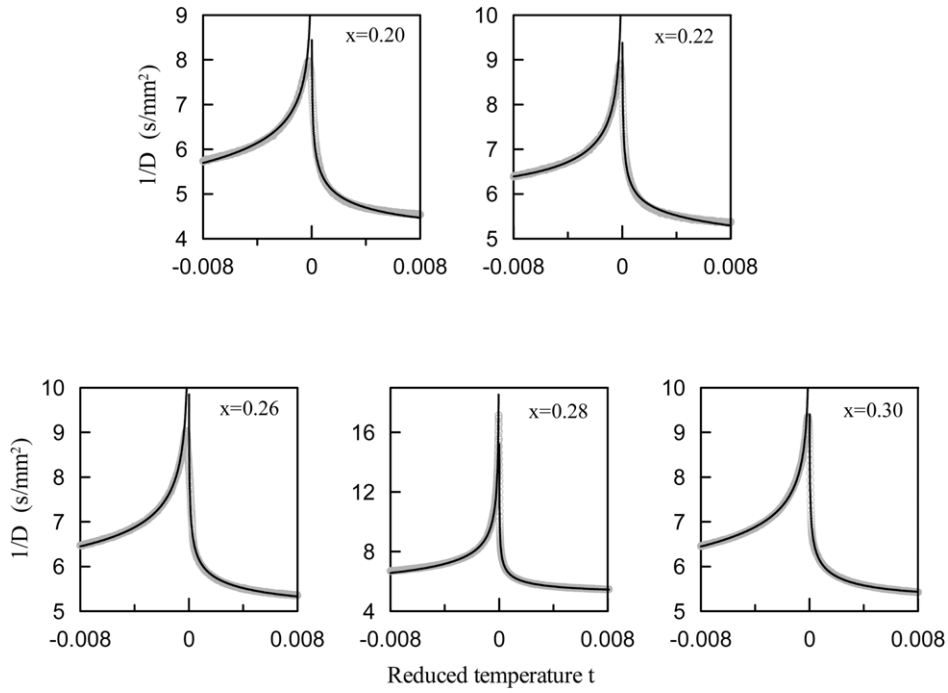


Figure 4. Experimental data (circles) for the inverse of thermal diffusivity as a function of the reduced temperature $t = (T - T_C)/T_C$. The lines represent the fits to equation (3).

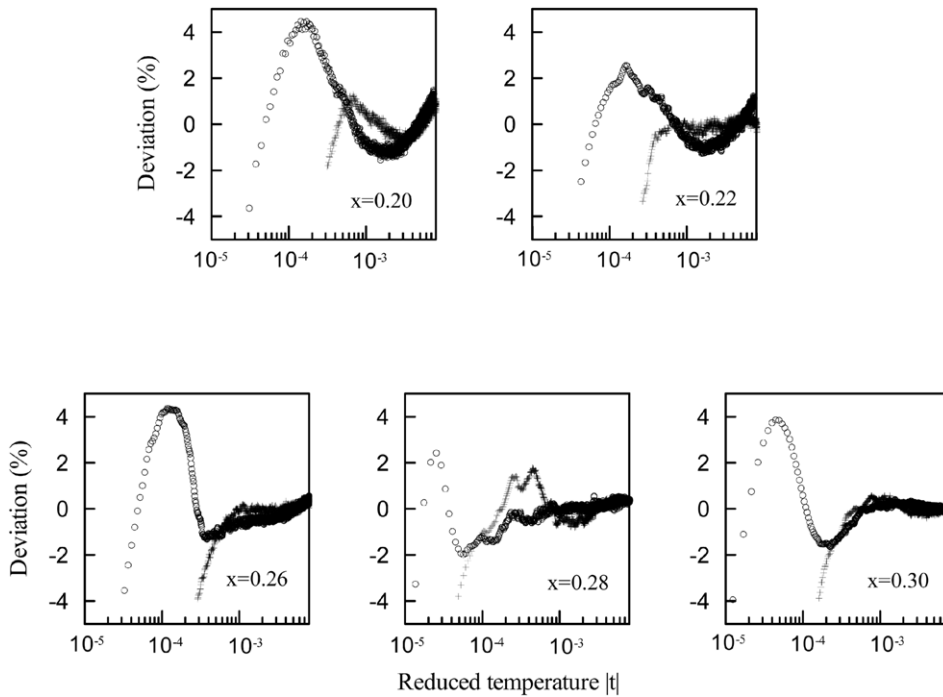


Figure 5. Deviation plots corresponding to the fits in figure 4. Open circles are for $T < T_C$ and crosses for $T > T_C$.

mixed, the thermal diffusivity is lowered, since the different size of these atoms enhances the phonon scattering process and therefore the phonon mean free path is reduced.

The shapes of the thermal diffusivity dips obtained for $x = 0, 0.15, 0.20, 0.22$ are similar to those commonly found for second order phase transitions in ferroelectrics or in magnetic systems. These features, together with the lack of thermal hysteresis, indicate that, indeed, there is a direct

second order transition from the paraelectric to the ferroelectric phase. In samples with $x = 0.26, 0.28,$ and 0.30 the shapes are typical second order but there is not a complete absence of hysteresis, which means that in this region we find a starting evolution from a second order character to a first order one while passing through the Lifshitz point. This changing character is fully developed in the samples with $x = 0.40$ and 1 (abrupt changes in the slope of the experimental curve at the

transition, thermal hysteresis, different shape on heating and cooling runs). It is worth noting that, unlike for the sample with $x = 1$, at $x = 0.40$ we cannot ascertain the presence of two transitions in thermal diffusivity measurements; better quality samples would be needed to study this matter in concentrations in between ($x = 0.60, 0.80$).

In order to study the critical behavior, one major concern is how close one can get to the critical temperature before entering the rounding zone in order to extract reliable information from the experimental curves. Order parameter fluctuations are important within a reduced temperature range marked by the Ginzburg criterion, which has been evaluated to be $\tau_G \approx 10^{-2}$ in this material [7]. First fluctuation corrections (Gaussian approximation) can be used to study critical behavior using experimental results for $t > \tau_G$, where the values of the critical exponent α are well known for different classes of universality. When approximating the critical temperature $t < \tau_G$, the interacting order parameter fluctuations are important and crossovers to other universality classes can be studied, for which renormalization group theory is needed.

In the pure sample $\text{Sn}_2\text{P}_2\text{S}_6$, the critical behavior studied by means of birefringence in the paraelectric phase was attributed to the UTL universality class ($\alpha = 0.5$ with logarithmic correction) [6], which was justified by the suppression of fluctuations by the long-range interactions. With that technique, only a reduced temperature range higher than 10^{-3} could be reached. Similar conclusions were obtained by Say *et al* [10] through the study of the spontaneous strains, but also on a temperature range not too close to the critical temperature. Thermal diffusivity measurements, which allowed us to get closer to the critical temperature ($t \approx 6 \times 10^{-4}$), showed that though a mean-field model could be acceptable in the temperature region outside that of critical fluctuations, it was at fault in the near vicinity of the critical temperature. First of all, it was not possible to fit simultaneously both ferroelectric and paraelectric phases, but a different fitting for each phase was needed. Besides, no good fittings to any universality class were obtained [28].

Concerning the doped samples $\text{Sn}_2\text{P}_2(\text{S}_{1-x}\text{Se}_x)_6$, while approaching the Lifshitz concentration, there was a higher deviation from a mean-field behavior and so a crossover to a more specific tricritical behavior was claimed [6]. Again, only reduced temperatures higher than 10^{-3} could be reached.

In the present study, we have been able to approach the critical temperature much more than in previous works, to the order of $t = 10^{-5}$ in all concentrations. Moreover, we have fitted both ferroelectric and paraelectric phases simultaneously. Accordingly, our experimental results allow us to put to test renormalization group theories concerning the different universality classes, which take into account long-range dipolar interactions, tricriticality, and the Lifshitz point.

For the pure ($x = 0$) and lightly doped ($x = 0.15$) samples no meaningful fittings to equation (3) have been obtained. Therefore, they cannot be safely attributed to a particular universality class. This means that there is not a clear dominant effect (short or long-range dipolar interactions, fluctuations, defects . . .).

On the other hand, it has been interesting to find that, as Se concentration is increased, the fittings to equation (3) improved and gave meaningful adjustable parameters. In order to interpret them, we looked at the same time at the values of the critical exponent α and the amplitude ratio A^+/A^- .

Concentration $x = 0.20$ is just a limiting case since it is the first concentration in which we can fit both branches simultaneously, but the quality of the fittings is poor so that we cannot obtain reliable conclusions on the universality class to which it belongs. Concerning the concentrations around the Lifshitz point ($x = 0.22, 0.26, 0.28$, and 0.30) the values of the critical exponent α fall between 0.21 and 0.34 . These values discard the possibility that the critical behavior is well described by the uniaxial tricritical Lifshitz universality class UTL (α should be around 0.5). As explained in section 1, if strong dipolar interactions were considered, the critical exponent should become 0.17 (uniaxial Lifshitz class UL). But for a Lifshitz class L, α has been theoretically found to be between 0.20 and 0.25 (depending on the first loop or second order approximation in the calculations). Our results support this last model, indicating that being a Lifshitz point is more relevant when describing the critical behavior than the long-range dipolar interactions of these uniaxial ferroelectrics or the nearness to a tricritical point. Regarding the amplitude ratio A^+/A^- , our fitted values range between 0.42 and 0.51 . These values are close to 0.35 , which is the value estimated in the second order approximation for a Lifshitz system without taking into account strong dipolar interactions. Hence, both the critical exponent and the amplitude ratio values lead to the conclusion that long-range interactions do not have a strong influence on the critical behavior in this system. This is related to the partial screening of the dipole-dipole interaction by charge carriers in the studied ferroelectric semiconductors.

5. Conclusions

Thermal diffusivity has been studied for the ferroelectric family $\text{Sn}_2\text{P}_2(\text{Se}_x\text{S}_{1-x})_6$ ($0 \leq x \leq 1$) through a high-resolution photopyroelectric technique which has allowed us to observe the change in character of the paraelectric to ferroelectric phase transition in the vicinity of the Lifshitz point ($x = 0.28$), as well as the appearance of an intermediate transition at high selenium concentrations ($x = 1$).

The description of the critical behavior of uniaxial ferroelectrics $\text{Sn}_2\text{P}_2(\text{Se}_x\text{S}_{1-x})_6$ in terms of the different universality classes and their underlying physical dominant effects (tricriticality, long-range dipole interactions and Lifshitz point) has been examined comparing experimental measurements in the very close vicinity of the critical temperature. The study reveals that for selenium concentrations around the Lifshitz point, long-range dipole interactions do not play a significant role and that the critical parameters are close to those of the Lifshitz universality class.

Acknowledgments

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