Journal of Alloys and Compounds 694 (2017) 808–814

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

In search of a tricritical Lifshitz point in $Sn_2P_2(S_{1-x}Se_x)_6$ doped with Pb, Ge: A critical behavior study

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A R T I C L E I N F O

Article history:
Received 30 May 2016
Received in revised form
6 October 2016
Accepted 8 October 2016
Available online 11 October 2016

Keywords:
Tricritical Lifshitz point
Ferroelectrics
Phase transitions
Critical behavior
Universality class

A B S T R A C T

A critical behavior study of $Sn_2P_2(S_{1-x}Se_x)_6$ has been undertaken for x = 0.28 (Lifshitz point) independently doped with Pb and Ge in search of the realization of a Tricritical Lifshitz point. The critical parameter α has been obtained from thermal diffusivity measurements performed with *ac* photopyroelectric calorimetry and its value compared with the different universality classes related to tricriticality and Lifshitz points. The evolution of the features of the experimental curves (position in temperature, shape, thermal hysteresis) has been compared with theoretical predictions related both to the stereoactivity of the metal cations in the studied samples and to the Blume-Emery-Griffith model with random field effects. A tricritical Lifhsitz point has been found for 5%Pb doping at $T_C = 259.12$ K, for which the universality class Lifshitz Tricritical LT has been unambiguously assigned as the obtained critical exponent $\alpha = 0.64$ is exactly the theoretical one. Higher dopant concentration (8%) induces a first order phase transition, further proving the presence of a tricritical point. The changes in the experimental curves agree with theoretical predictions. Impurity of Ge slightly increases the critical temperature from 281.31 K to 284 K due to the strengthening of the stereoactivity but changes neither the character of the transition nor the universality class, as it is still Lifshitz L, with critical exponent $\alpha = 0.25$.

1. Introduction

The phase diagram of $Sn_2P_2S_6$ as a function of temperature *T*, pressure *p*, and doping with different species *x* has been an object of study for more than 20 years. From a practical point of view, the family has promising photorefractive and optical applications [1–3] while from the condensed matter physics perspective, it presents a rich variety of transitions as well as different special multicritical points: Lifshitz point LP, Tricritical points TCP, tricritical Lifshitz point TCLP [4]. The Lifshitz point is the one at which the line of continuous ferroelectric to paraelectric direct transitions splits into two lines, appearing an incommensurate phase between the paraelectric at higher temperatures and the ferroelectric commensurate at lower ones. The latter are first order transitions while the previous ones are continuous. This is realized in practice with Se as dopant in the parent compound $Sn_2P_2(S_{1-x}Se_x)_6$ with $x \approx 0.28$. A tricritical point TCP has been theorized to be at $x = 0.6$ but it is a virtual point as the Lifshitz point takes precedence [4–6].

On the other hand, a special critical point has been found in $Sn_2P_2S_6$ applying pressure. There has been some discussion in literature along the years about the possibility that this point be a TCP or a LP [5,7,8] but neutron diffraction measurements have ruled out the presence of an incommensurate phase (studied between 0.18 and 0.6 GPa), settling this matter in favour of a simple TCP [9]. Recent experiments using ultrasound velocity [10] and optical birefringence [11] have confirmed this matter, obtaining a TCP at $p \approx 0.4$ GPa, $T \approx 250$ K. X-ray scattering data also showed a complete absence of incommensurate phase up to 1 GPa [12]. Theoretical considerations based on the comparisons with the Blume-Emery-Griffith model also discarded the possibility of finding a Lifshitz point LP on the *T-p* diagram of $Sn_2P_2S_6$ [10]. In Ref. [12] it is pointed out that a small jump in the lattice parameter and monoclinic angle is found when applying 1.2 GPa and it is suggested that the point reported in Ref. [7] at $p \approx 0.18$ GPa, $T \approx 296$ K could be the TCP. But, as pointed above, ref [10] and [11] have lately proved that this only happens at $p \approx 0.4$ GPa, $T \approx 250$ K.

Several papers have been devoted to the quest of finding the conditions in the phase diagram (*T*, *p*, *x*) to obtain a tricritical Lifshitz point TCLP [5,13,14]. This is the point where the LP and a TCP

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http://dx.doi.org/10.1016/j.jallcom.2016.10.071
0925-8388/

would merge, which has been theorized to be found in the more complex phase diagram (T, p, x, y) taking into account two dopants, in $(Pb_ySn_{1-y})_2P_2(S_{1-x}Se_x)_6$. It has been proposed that it could be found at $T = 225$ K, $p = 0.28$ GPa, $x = 0$, $y = 0.12$ [14] but has not been experimentally proved yet.

The effects that different kind of dopants have in the phase diagram of $Sn_2P_2S_6$ have been increasingly studied in the last years (Se and Te in the place of S, Pb and Ge in the place of Sn and even Sb taking the place of P). Doping with Se, Pb and Ge has very relevant consequences while Te and Sb introduce very small or negligible changes [4,15–22]. The stereoactivity of the Sn^{2+} cation $5s^2$ electron lone pair is responsible for the ferroelectric transition. There is an antibonding mixing of Sn 5s and S 3p orbitals, which in its turn develops a bonding interaction with the Sn 5p orbitals, generating lower-energy filled states Sn 5p + (Sn 5s-S 3p). This formation of the Sn^{2+} lone pair electron cloud together with the deformation of the nearest polyhedron formed by the sulfur atoms determines the origin of the spontaneous polarization. The hybridization becomes stronger at the ferroelectric transition, increasing the spontaneous polarization [23,24]. Its substitution by Ge enhances the stereoactivity of the cation sublattice, because of the smaller energy distance between Ge 4s and S 3p states, increasing the critical temperature and sharpening the transition [17,19]; on the other hand, the addition of Pb first lowers and then frustrates the ferroelectric transition as concentration is increased [4,15,16] because of the bigger difference between Pb 6s and S 3p states would make the hybridization weaker.

Se, on the other hand, substitutes S, having a more indirect role in the stereoactivity of the crystal. The chemical bond covalency increases with this substitution, weakening the stereoactivity of the Sn^{2+} ions. This results in the decrease of the critical temperature, which would eventually lead to a virtual TCP which has been predicted at x ≈ 0.6 and T ≈ 240 K [4].

The evolution of the character and critical behavior of the transitions with doping has been thoroughly studied. The character (first or second order) has been studied either by the evaluation of the sign and value of the parameter of fourth order in the expansion of the Landau thermodynamic potential or by the presence of hysteresis in experimental measurements; the critical behavior has been studied comparing the critical parameters found with the Landau mean-field theory or with the different universality classes predicted by renormalization group analysis. Let's bear in mind that each universality class corresponds to a particular hamiltonian in which different physical mechanisms are taken into account; to each universality class corresponds a different set of the critical parameters α (associated to specific heat), β (associated to spontaneous polarization) and γ (associated to the inverse of dielectric susceptibility) through the equations

$$c_p(T) \sim A^{\pm}\left|t\right|^{-\alpha} \quad \left(A^{-}\ for\ T < T_C, A^{+}\ for\ T > T_C\right) \tag{1}$$

$$P_S(T) \sim \left|t\right|^{-\beta} \quad (T < T_C), \tag{2}$$

$$\chi^{-1}(T) \sim \left|t\right|^{\gamma} \quad (T > TC), \tag{3}$$

which are fulfilled in the critical region, where fluctuations of the order parameter are relevant. Several research groups have obtained the theoretical values of the critical parameters for the different universality classes which are appropriate to study this family of uniaxial ferroelectrics with so complex a phase diagram, taking into account possible Lifshitz, tricritical, Lifshitz tricritical points, with or without dipolar interactions. A summary of all classes can be found in Ref. [25] but there are some other calculations performed to improve the accuracy of the values of the critical exponents, especially for the Lifshitz class [26–29]. It is worth noting that the best parameter to discriminate among models is α as it changes more from one universality class to another one, taking different values for the Tricritical class T (0.5 with a logarithmic correction), Uniaxial Tricritical UT (0.5), Lifshitz L (0.25), Uniaxial Lifshitz UL (1/6), Tricritical Lifshitz LT (9/14); on the other hand, β changes much less among the classes. Besides, β and γ are obtained only from the study of one phase while, in order to obtain α, information from both phases (above and below T_C) should be used; strict application of the modern critical behavior theory demands that certain theoretical constraints must be taken into account when performing the fittings to extract α [30–33], making the task more difficult but more reliable when a good fit is found.

Experimentally, the critical exponents α and β have been evaluated for these ferroelectrics by fitting different kind of physical variables which behave in the critical region as the ones in Eqs. (1) and (2): neutron scattering [9] and optical birefringence [34,35] to obtain β, the latter's derivative [35], ultrasonic velocity [36] and the inverse of thermal diffusivity [6,16,19,37,38] to extract α but only with this last variable the strict procedure pointed out in the previous paragraph has been undertaken. In particular, previous studies on the continuous transitions in $Sn_2P_2(S_{1-x}Se_x)_6$ from x = 0 to 1 [6,38] showed that x = 0.28 corresponded to the Lifshitz class L, discarding other classes and in particular the uniaxial Lifshitz, meaning that long-range dipolar interactions do not play a significant role at this concentration and that, instead, fluctuations of the order parameter are responsible for deviating the system from a mean field model. Now, the aim of this work is to pursue the possible localization of a tricritical Lifshitz point starting from the Lifshitz concentration, adding another dopant which can have an influence on the stereoactivity of the material, such as Pb and Ge. We will study the changes in character and critical behavior of the ferroelectric transition, focusing on the possible appearance of a Lifshitz Tricritical universality class or a related one by studying the critical parameter α.

2. Samples and experimental techniques

Single crystals of $Sn_2P_2(S_{0.72}Se_{0.28})_6$ additionally doped with 5% Pb, 8% Pb and 5% Ge (atomic percentages) have been grown using a vapor-transport method in an evacuated quartz tube using I_2 as a transport agent. The synthesis of the starting material in the polycrystalline form was carried out using high-purity elements Sn (99.99%), P (99.999%), S (99.99%), Se (99.99%), Pb (99.99%) and Ge (99.999%), also in atomic percentage. Required amount of tin, phosphorous, sulfur, selenium, lead or germanium was placed into quartz tube for further homogenization at 650 C during one week. After, the recrystallization by vapor transport between hot zone at 650 C and cool zone at 630 C has taken three days. At next stage the cool zone was cleaned by heating and further this zone has been cooled to 615 C and kept at this temperature till appearance of visually observed crystal nucleus. From this moment the monocrystal growth was started with duration near one month. At finish of growth process the hot zone of quartz tube was absolutely clean, what give evidence about full mass transport and growth of monocrystal with needed stoichiometry.

It is well known that Pb can completely substitute Sn while Ge can only be introduced up to a certain quantity due to its electronic properties [24]. This explains why it is not possible to grow $Sn_2P_2(S_{0.72}Se_{0.28})_6$ with higher Ge contents. The crystals have been characterized by X-ray diffraction (XRD) technique, both to check their quality and to orient the samples. For all three cases, very sharp and unique diffraction lines were obtained confirming the good crystal quality of the samples, without the presence of any phases. The two crystals doped with Pb and the one doped with Ge were oriented in the [001] and [100] crystallographic directions, respectively.

The variable measured in this study is thermal diffusivity D, for which thin plane-parallel slabs were cut in the perpendicular direction to that found from XRD investigations and carefully polished. The samples thicknesses were as follows: 0.535 mm, 0.530 mm and 0.495 mm for $Sn_2P_2(S_{0.72}Se_{0.28})_6$+5%Pb, $Sn_2P_2(S_{0.72}Se_{0.28})_6$+8%Pb and $Sn_2P_2(S_{0.72}Se_{0.28})_6$+5%Ge, respectively. In order to perform a high resolution temperature sweep of D across the paraelectric to ferroelectric phase transition, a combination of an *ac* photopyroelectric technique in the back-detection configuration with $LiTaO_3$ as a sensor and a closed cycle He cryostat has been employed. The detailed methodology of the measurements performed can be found in Ref. [6] and references therein. The wide temperature ranges have been measured with a rate of 0.1 K/min. The precise shape of the thermal diffusivity anomaly around T_C has been provided by a controlled continuous temperature variation as slow as 10 mK/min and thermal hysteresis measurements have been performed with rates as low as 2.5 mK/min. The experimental curves shown in all graphs are the ones obtained experimentally, without any fitting or treatment. In the continuous runs, the relative resolution of the points is ± 0.0001 mm^2/s in D and ± 0.001 K in T, retrieving the precise shape of the thermal diffusivity as a function of temperature, especially around the phase transition point.

3. Experimental results and fittings

Fig. 1 shows the thermal diffusivity of the three samples under study. It is worth bearing in mind that the critical temperature for the Lifshitz concentration $Sn_2P_2(S_{0.72}Se_{0.28})_6$ was found to be 281.31 K and that its thermal diffusivity was the sharpest dip in the series $Sn_2P_2(S_{1-x}Se_x)_6$ $x = 0–1$ [6]. The addition of Pb weakens the stereoactivity of the material, reducing the temperature of the transition to 259.12 K for 5% and then to 251.96 K for 8%. The dip is smeared and broadened with respect to the published one for $Sn_2P_2(S_{0.72}Se_{0.28})_6$, in a similar behavior as in the series $(Pb_ySn_{1-y})_2P_2S_6$ [16]. On the contrary, Ge enhances the stereoactivity and that's why the critical temperature increases up to 284 K with a broadened dip with respect to the Lifshitz concentration but still very sharp. Again, this behavior resembles the one obtained in

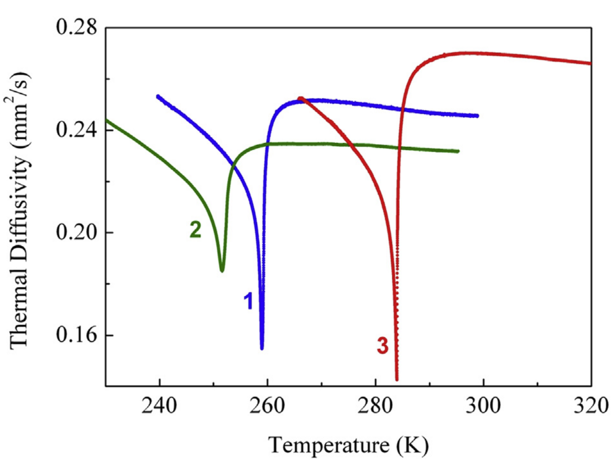

Fig. 1. Thermal diffusivity as a function of temperature in the vicinity of the critical temperature for $Sn_2P_2(S_{0.72}Se_{0.28})_6$ doped with 5% Pb (curve 1), 8% Pb (curve 2), 5% Ge (curve 3).

$Sn_2P_2S_6$ doped with Ge [19].

The possible thermal hysteresis has been checked in detail to study the character of the transitions by performing heating and cooling runs with decreasing rates of 20, 10, 5, 2.5 mK/min (see Fig. 2). The samples doped with 5%Pb and 5%Ge show the same behavior as the undoped $Sn_2P_2(S_{0.72}Se_{0.28})_6$: they are in the verge of changing their character from second order to first order as we don't find a perfect superposition of the heating and cooling runs as when they are continuous transitions (see Ref. [6] for the comparison in $Sn_2P_2(S_{1-x}Se_x)_6$ of the behavior among the samples with continuous transitions, those with first order ones and those with dopings around the Lifshitz concentration) but there is not a really clear hysteresis. The asymptotic behavior shown in Fig. 2a and c indicates a difference in the critical temperatures of around 0.14 K, nearly as in $Sn_2P_2(S_{0.72}Se_{0.28})_6$. On the other hand, the sample with 8%Pb has clearly crossed the border (Fig. 2b) as it happened, for instance, with $Sn_2P_2(S_{0.6}Se_{0.4})_6$ [6]. The asymptotic value for the difference in critical temperature in heating and cooling runs is 0.28 K, indicating that, with this doping, the transition is already a first order one. This would indicate the presence of tricriticality between 5% and 8% Pb.

In order to ascertain what kind of tricritical point is being crossed here, we have investigated the evolution of the universality class from the Lifshitz one (L) obtained in Ref. [6] for $Sn_2P_2(S_{0.72}Se_{0.28})_6$. The inverse of the thermal diffusivity behaves critically as the specific heat c_p if thermal conductivity K does not present a singularity at the transition (as is the case in this ferroelectric family [6,37,39]), because they are related by the equation

$$c_p = \frac{K}{\rho D} \tag{4}$$

where ρ stands for density.

And the equation used to perform the fittings of the second order phase transitions in the close neighborhood of the critical temperature has been the well known

$$\frac{1}{D} = B + Ct + A^{\pm}|t|^{-\alpha}\left(1 + E^{\pm}|t|^{0.5}\right) \tag{5}$$

Superscripts + and − stand for $T > T_C$ and $T < T_C$ respectively. As explained elsewhere [38], 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 states that constant B needs also be the same. These are the strict conditions mentioned in the introduction to correctly perform these fittings. The experimental data were simultaneously fitted for $T > T_C$ and $T < T_C$ with a non-linear least square routine using a Levenberg-Marquardt method. First of all, we selected a fitting range close to the transition while avoiding the rounding, and kept fixed the value of T_C. We obtained a first fitting without the correction to scaling term and obtained a set of adjusted parameters. Afterwards, 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}. The next step was introducing the correction to scaling term trying to improve the fitting. 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 values 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. The values of the uncertainties in all the parameters are crucial to evaluate the quality of the fitting [31].

Fig. 3 contains the experimental curves and the theoretical fittings for 5%Pb and 5%Ge together with the deviation plots, which

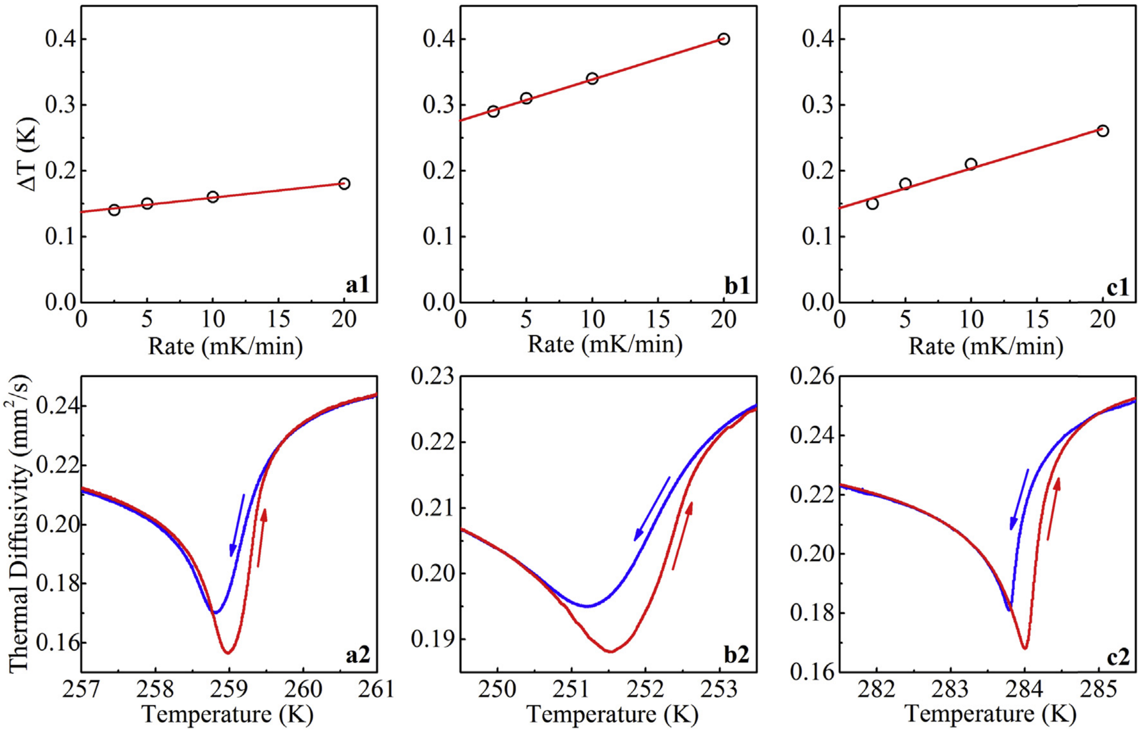

Fig. 2. Thermal hysteresis. Above: Difference in the critical temperature in heating and cooling runs as a function of temperature rate; the circles are the experimental values, the straight lines the linear fittings. Below: Shape of the thermal diffusivity curves on heating and cooling for a temperature rate of 10 mK/min. Labels are as follows: a1 and a2 are for $Sn_2P_2(S_{0.72}Se_{0.28})_6$ doped with 5% Pb, b1 and b2 with 8% Pb, c1 and c2 with 5% Ge.

show the difference between the experimental points and the fitted ones in percentage. The number of experimental points in those curves is of the order of five thousand points. Table 1 contains the fitted parameters with their errors (which are extremely low) as well as the fitting range and the coefficient of determination R^2, which is a measure of the quality of the fitting. All elements combined, the fittings are of a very high quality, ensuring that the conclusions based on them have a sound physical meaning. Of course, no fitting has been performed for 8%Pb as this analysis only makes sense for second order phase transitions. The value of the critical exponent α for 5% Pb is 0.64 (which corresponds nicely with the universality class Lifshitz Tricritical LT for which $\alpha_{Theoretical} = 0.64$) while for 5% Ge is 0.25, still within the Lifshitz class L. The ratio of the critical parameters A^+/A^- is 0.63 and 0.49, respectively.

A last comment about the validity of these critical parameters. Synchrotron X-ray diffraction studies of $Sn_2P_2S_6$ near the ferroelectric phase transition have revealed the presence of two components in the critical scattering (two-length-scale behavior), as described in some other continuous transitions [40]: there is an additional sharp component in the diffraction spectra (besides the common broad peak) which comes from a very thin skin layer of the material near the surface and whose critical behavior has specific characteristics as this zone is strained and different to the bulk; some particular conditions must be fulfilled for this sharp component to appear. In our measurements, the contribution of this skin layer is negligible as we measure the through-thickness thermal diffusivity of the samples (which have around 500 μm) while the skin layer is very thin. According to XPS data, the oxygen linked to the oxidized surface of the sample is only 50 nm deep [41]. To our knowledge, no two-length scale behavior has ever been observed in literature when studying the critical behavior of phase transitions using thermal parameters such as specific heat or thermal diffusivity in any material, as they are volume measurements.

4. Discussion

Not only experimental work can be found in literature on the properties of $Sn_2P_2(S_{1-x}Se_x)_6$ but theoretical as well. An ab-initio effective Hamiltonian model has been developed to account for the dynamic and thermodynamic properties of $Sn_2P_2S_6$ in a broad temperature range based on a three-well local potential for order parameter fluctuations [42]. On the one hand, the application of this model has allowed to predict a specific heat anomaly with features comparable to the ones obtained experimentally [43]. On the other, this potential can be related to the Blume-Emery-Griffth model (BEG) for analysis of systems with pseudospins 0, ±1 and, as such, has been applied to qualitatively explain the influence of Pb when substituting Sn on the ferroelectric properties of $(Pb_ySn_{1-y})_2P_2S_6$ [44]. Besides, a joint BEG-ANNNI (axial-next-nearest-neighbor Ising model) has been theoretically applied to consider a possible TCLP in a system with a three-well potential with the result that the LPs line terminates at the TCLP on pressure application [45]. The application of this model to $Sn_2P_2S_6$ with applied pressure implies that the second order ferroelectric phase transition would diminish its temperature and that a TCP would be reached, as it has been experimentally shown in the T-p phase diagram [10]. Pressure reduces the stereoactivity of the cation sublattice and, as a consequence, the depth of the side wells in the local three-well potential are also reduced, decreasing the critical temperature till the character is changed to first order.

The addition of Pb has the effect of diluting the stereoactivity as it weakens the bonding hybridization responsible for ferroelectricity, showing that introducing this alien atom creates a “chemical pressure” with similar effects to the mechanical pressure. In fact,

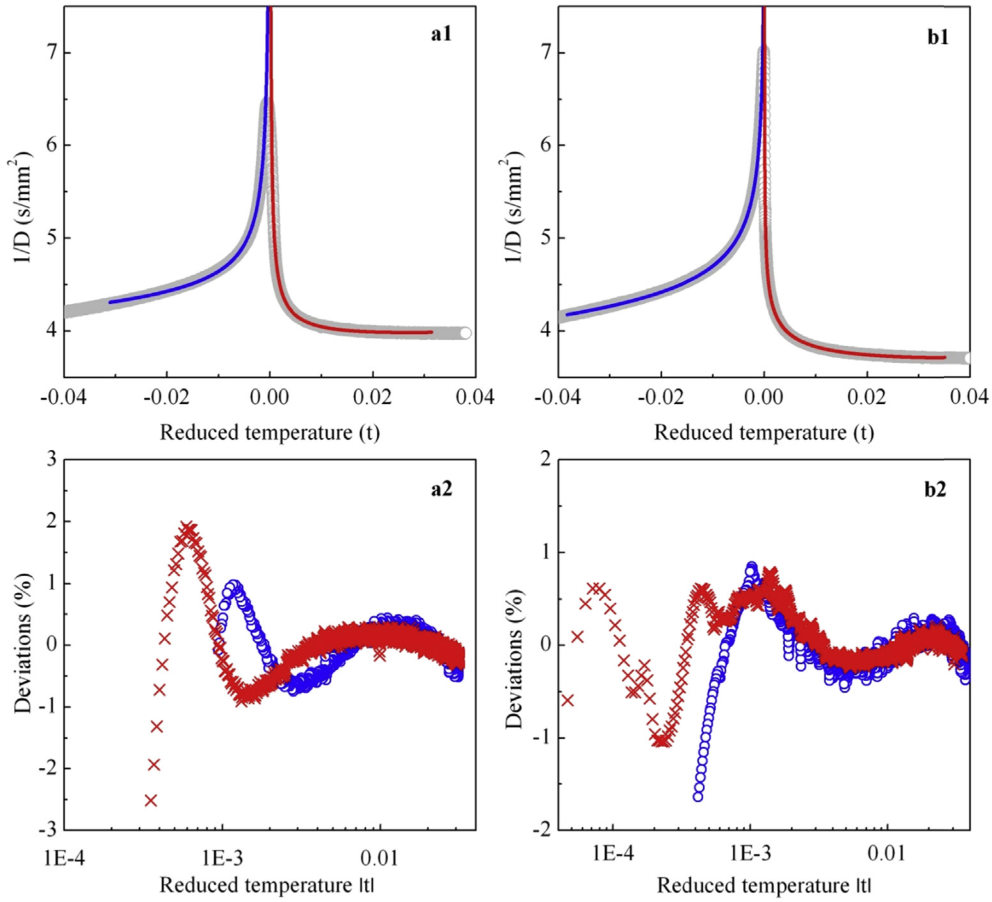

Fig. 3. Above: Experimental data (circles) for the inverse of thermal diffusivity as a function of the reduced temperature for $Sn_2P_2(S_{0.72}Se_{0.28})_6$ doped with 5% Pb (a.1) and with 5%Ge (b.1). The continuous lines represent the fits to Eq. (5). Below: Deviation plots corresponding to the fits shown above. Open circles are for $T < T_C$ and crosses for $T > T_C$.

the description of the properties of the $(Pb_ySn_{1-y})_2P_2S_6$ system has been successfully carried out within the framework of the BEG model taking into account the presence of random fields created by the addition of Pb [44], which predicts that the character of the transitions must change from continuous to first order as temperature is decreased; besides, smearing of the transitions should take place because of the increasing random field [44,46]. Finally, the addition of Se to $Sn_2P_2S_6$ also reduces the critical temperature (though the effect on stereoactivity is much smaller than with Pb) but the random field effects are not appreciable as there is no smearing in the transitions [6].

Thus, taking into account the combined effects of Pb and Se and the predictions of the theoretical models, we can expect that a TCLP is reachable if Pb is introduced in $Sn_2P_2(S_{0.72}Se_{0.28})_6$, that is, starting from the LP. And this is what our experimental results are proving. The addition of 5%Pb changes the critical behavior of the transition from a Lifshitz class L to a Lifshitz Tricritical class LT with $\alpha = 0.64$ (the theoretical value is also 0.64); the quality of the fitting is extremely good with very small errors in the parameters (see Table 1) and small deviations (see Fig. 3a). The tricritical classes T or UT are discarded because their theoretical values are 0.5 with a logarithmic correction and 0.5, respectively, so this transition is indeed related to the Lifshitz point. We have checked the possibility of obtaining fittings with these parameters but it has not been possible, all of the trials have been unsuccessful. Another possibility is having a uniaxial Lifshitz class UL ($\alpha_{\text{Theoretical}} = 1/6$) or a uniaxial tricritical Lifshitz point (α should be 0.5 with another logarithmic correction); trials have been undertaken to fit the curve to both models but, again, they have been fruitless. This means that we are facing a tricritical point where the dipolar interactions are not relevant but the fact that it is a Lifshitz point, where fluctuations of the order parameter are the main cause of deviation from the mean field model. In our fittings, we also obtain the ratio of the critical coefficients A^+/A^- but, unfortunately, they have not been theoretically calculated by renormalization group theory for most of these universality classes yet. Only the value for the Lifshitz class L is given, which ranges between 0.30 and 0.35 [28]. The experimental value obtained for $Sn_2P_2(S_{0.72}Se_{0.28})_6$ was 0.42 [6] and we have now found for the sample doped with 5%Pb a higher value of 0.63. New theoretical developments are needed in order to know if this is sensible or not.

Additional evidence that this is a tricritical point is given by the fact that at a higher doping (8%Pb) the character of the transition is clearly first order, as obtained from the hysteresis study (see Fig. 2b) while at 5% it is on the verge of changing from second order to first order (see Fig. 2a). Both transitions are smeared compared to the sample without lead, confirming the theoretical predictions of the BEG model with random fields created by the dopant.

Finally, the study of the sample doped with 5%Ge confirms the different role played by Pb and Ge, even at the Lifshitz point; due to the strengthening of the hybridization responsible for ferroelectricity which takes place with the addition of Ge [17–19], the temperature of the transition is raised, but only 2.7 K. The hysteresis study confirms that it is a transition with the same features as the Lifshitz concentration, about to change character (see Fig. 2c) and the critical exponent agrees well with the Lifshitz class

Table 1
Results of the fitting of the inverse of thermal diffusivity $1/D$ using Eq. (5). The fitting parameters (α, A^+, A^+/A^-, T_C, B, C, $E^{\pm}$) are shown together with the fitted range and the coefficient of determination R^2.

	α	A^+ s/mm^2	A^+/A^-	T_C K	Fitted range $\lvert t \rvert$ $T > Tc$	Fitted range $\lvert t \rvert$ $T < Tc$	B s/mm^2	C s/mm^2	E^+	E^-	R^2
5%Pb	0.638 ± 0.006	0.0140 ± 0.0008	0.631 ± 0.001	259.122 ± 0.001	3.54×10^{-4}–3.14×10^{-2}	9.45×10^{-4}–3.11×10^{-2}	3.85 ± 0.02	2.89 ± 0.05	−3.8 ± 0.7	9.5 ± 0.9	0.9988
5%Ge	0.252 ± 0.001	0.269 ± 0.004	0.493 ± 0.005	283.995 ± 0.001	4.69×10^{-5}–3.50×10^{-2}	4.18×10^{-4}–3.83×10^{-2}	2.84 ± 0.01	2.98 ± 0.04	1.23 ± 0.06	0.87 ± 0.01	0.9997

($\alpha = 0.25$) while the critical ratio is 0.49, somewhat higher than the theoretical value but close to the one obtained for the undoped sample [6]. The fittings are again very good (see Table 1 and Fig. 3b) and, as a final check, trials have been performed to fit the curve to any of the other relevant universality classes, without any success. Thus, the Lifshitz character is maintained in this sample.

It would be desirable to corroborate these results studying the critical behavior of other physical variables for whom the critical exponents of the universality classes have been theorized; this would be the case of, for instance, specific heat or dielectric susceptibility; nevertheless, it must be pointed out that high resolution measurements performed at very low temperature rates are needed to extract with detail the shape of the transitions and fit them to the theoretical model.

5. Conclusions

A tricritical Lifhsitz point has been found in $Sn_2P_2(S_{0.72}Se_{0.28})_6$ doped with 5%Pb at $T_C = 259.12$ K, fulfilling the predictions of the BEG model with random field proposed in literature. The first prediction says that a Lifshitz point line will terminate in a Tricritical Lifshitz point upon pressure application (chemical doping can have an equivalent effect to mechanical pressure) with a reduction in temperature; the second prediction states that the transitions will be smeared while changing the character. The universality class Lifshitz Tricritical LT has been unambiguously assigned to this transition as the obtained critical exponent α is the theoretical one (0.64). Higher dopant concentration (8%) induces a first order phase transition, further proving the presence of a tricritical point. On the other hand, doping $Sn_2P_2(S_{0.72}Se_{0.28})_6$ with Ge slightly increases the critical temperature from 281.31 K to 284 K due to the strengthening of the stereoactivity but changes neither the character of the transition nor the universality class, as it is still Lifshitz class L.

Acknowledgements

This work have been supported by UPV/EHU (UFI11/55). The authors thank for technical and human support provided by SGIker of UPV/EHU. V. Shvalya thanks the Erasmus Mundus programme "ACTIVE" for his grant.

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