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Lattice thermal conductivity of $Pb_{1-x}Sn_xTe$ solid solutions in the vicinity of the topological phase transition

E.I.Rogacheva, G.O.Nikolaenko, O.N.Nashchekina, G.V.Lisachuk

National Technical University "Kharkiv Polytechnic Institute",
2 Kyrpychova Str., 61002 Kharkiv, Ukraine

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The discovery of topological crystalline insulators (TCIs) with a metallic 2layer on the surface of a band-gap crystal and the prospects of their application in spintronics and quantum computation stimulate studies of the mechanisms of the transition to the TCI state. The semiconductor $Pb_{1-x}Sn_xTe$ solid solutions in the composition range corresponding to the inverted band structure were among the first discovered TCIs. One can suggest that due a strong electron-phonon interaction characteristic of these materials, the formation of a TCI layer is accompanied by some change in the properties determined by the lattice subsystem of the crystal. We measured the dependences of the lattice thermal conductivity λ_L of $Pb_{1-x}Sn_xTe$ on x in the vicinity of the TCI transition at different temperatures (170–300 K). In the $\lambda_L(x)$ isotherms, we observed two peaks near $x = 0.61$ and $x = 0.63$, which evidences that the TCI transition consists of at least two stages. We suggest that one peak corresponds to the band inversion point and the other is associated with a structural self-organization taking place in the crystal, and either stimulates or accompanies the TCI transition. Thus, the transition to the TCI state in $Pb_{1-x}Sn_xTe$ is accompanied by changes in the lattice subsystem of the crystal.

Keywords: $Pb_{1-x}Sn_xTe$, topological crystalline insulator, band inversion, lattice thermal conductivity.

Граткова теплопровідність твердих розчинів $Pb_{1-x}Sn_xTe$ поблизу топологічного фазового переходу. *О.І.Рогачова, Г.О.Ніколаєнко, О.Н.Нащекіна, Г.В.Лисачук*

Відкриття топологічних кристалічних ізоляторів (ТКІ) з металевим шаром на поверхні заборонено-зонного кристала та перспективи їх застосування у спінтроніці та квантових обчисленнях стимулюють дослідження механізмів переходу до ТКІ-стану. Одними з перших відкритих ТКІ були напівпровідникові тверді розчини $Pb_{1-x}Sn_xTe$ в області складу, що відповідає інвертовано-зонній структурі. Можна припустити, що через сильну електрон-фононну взаємодію, характерну для цих матеріалів, утворення шару ТКІ супроводжується деякою зміною властивостей, що визначаються гратковою підсистемою кристала. Виміряно залежності теплопровідності гратки λ_L $Pb_{1-x}Sn_xTe$ від x в околі переходу ТКІ за різних температур (170–300 К). На ізотермах $\lambda_L(x)$ спостерігаємо два піки поблизу $x = 0,61$ та $x = 0,63$, що свідчить про те, що перехід ТКІ складається принаймні з двох етапів. Ми припускаємо, що один пік відповідає точці інверсії смуги, а інший пов'язаний зі структурною самоорганізацією, що відбувається в кристалі, і або стимулює, або супроводжує перехід ТКІ. Таким чином, перехід до стану ТКІ в $Pb_{1-x}Sn_xTe$ супроводжується змінами граткової підсистеми кристала.

1. Introduction

The $Pb_{1-x}Sn_xTe$ semiconductor solid solutions belong to the materials widely used in infrared sensors, photoresistors, thermoelectric devices, etc. [1–3]. Also, these alloys are interesting model materials for

solid state physics because of a high sensitivity of their energy band structure to changes in external parameters, including composition. As x increases, the band gap E_g becomes narrower, and at a certain critical composition x_c, depending on temperature, a gapless state occurs and the conduction and valence bands invert at the L_6 point of the Brillouin zone [4, 5]. In [6], the presence of a thermodynamic phase transition at x_c was registered by measuring the dependence of heat capacity on x in the vicinity of x_c.

The interest in studying the band inversion in $Pb_{1-x}Sn_xTe$ has increased sharply after it was found by the angle-resolved photoemission spectroscopy (ARPES) method [7–9] that near x_c, not only does the band inversion occur, but also these materials become topological crystalline insulators (TCIs), which are characterized by the simultaneous existence of a metallic Dirac-like surface states topologically protected by mirror symmetry and semiconducting bulk states [10]. TCIs, as well as other types of topological insulators, are currently considered as promising materials for spintronics, quantum computation and thermoelectrics [10, 11].

A question arises whether the band inversion and a topological quantum transition occur at the same composition (x) of the $Pb_{1-x}Sn_xTe$ solid solutions. In the available works on the TCI transition in $Pb_{1-x}Sn_xTe$, the exact compositions at which transitions occur were not determined. That is why, to answer the question above, it is necessary to carry out detailed studies of the dependences of various properties on the composition in the vicinity of the critical point x_c. Because of the close interdependence between the electronic and lattice subsystems of the crystal and the strong electron-phonon interaction characteristic of the $Pb_{1-x}Sn_xTe$ solid solutions, the transition to the inverted state must be accompanied by changes in the lattice subsystem of the crystal (including the crystal structure) and manifested through not only the electronic but also the lattice properties. With increasing temperature, the contribution of the electron-phonon interaction increases.

The goal of this work is to investigate the phenomena that accompany the phase transition from a trivial phase to a topological crystalline insulator by measuring the dependences of the lattice thermal conductivity λ_L on composition x in the vicinity of the critical point x_c in the temperature range of 170–300 K.

2. Experimental

Polycrystalline samples of $Pb_{1-x}Sn_xTe$ alloys in the concentration range $x = 0.59$–0.68 were synthesized by fusing the starting elements in evacuated quartz ampoules at a temperature of 1240 K with a subsequent homogenizing annealing at 990 K for 200 h. The chemical composition and homogeneity of the samples were characterized by electron-probe microanalysis using a scanning electron microscope (SE3M) JSM6390LV with Energy-Dispersive X-ray (EDS) spectrometer X-max N 50. The results of microanalysis showed that the samples were homogeneous and their chemical composition corresponded to the intended one with an error not worse than $\Delta x = \pm 0.002$. Thermal conductivity λ was measured in the temperature range of 170–300 K by a dynamic calorimeter method in the monotonic heating regime on an IT-λ-400 device using hot-pressed (at 650 K under pressure 0.4 GPa) cylindrical specimens with a diameter of 15 mm and a length of 5.5 mm made from cast ingots and subjected to annealing at 720 K for 250 h. λ_L was separated from λ by subtracting the electronic component λ_x, which, in turn, was calculated using the Wiedemann-Franz law. The law was applicable because the measurements were carried out at temperatures above the Debye temperature. The electrical conductivity σ was measured using the van der Pauw method. The measurement error of λ and σ did not exceed 5 %.

3. Results and discussion

In Fig. 1, a,b, the $\lambda(x)$ and $\lambda_L(x)$ isotherms plotted on the basis of the temperature dependences $\lambda(T)$ are shown. As is seen, at all temperatures, there is a diffuse peak in the $\lambda(x)$ isotherms in the vicinity of $x = 0.62$. However, after subtracting the electronic component λ_x from the total thermal conductivity λ using the Wiedemann-Franz law, we obtain the composition dependence $\lambda_L(x)$ with two clear peaks with the maxima near $x = 0.61$ and $x = 0.63$ at all studied temperatures. At $T < 250$ K, the peaks partially overlap.

The presence of two peaks indicates that the transition to the TCI state occurs in at least two stages, each of which corresponds to a certain phase transition. The first peak can be attributed to the band inversion at the L_6 point of the Brillouin zone [4, 5], if we assume that topologically protected by

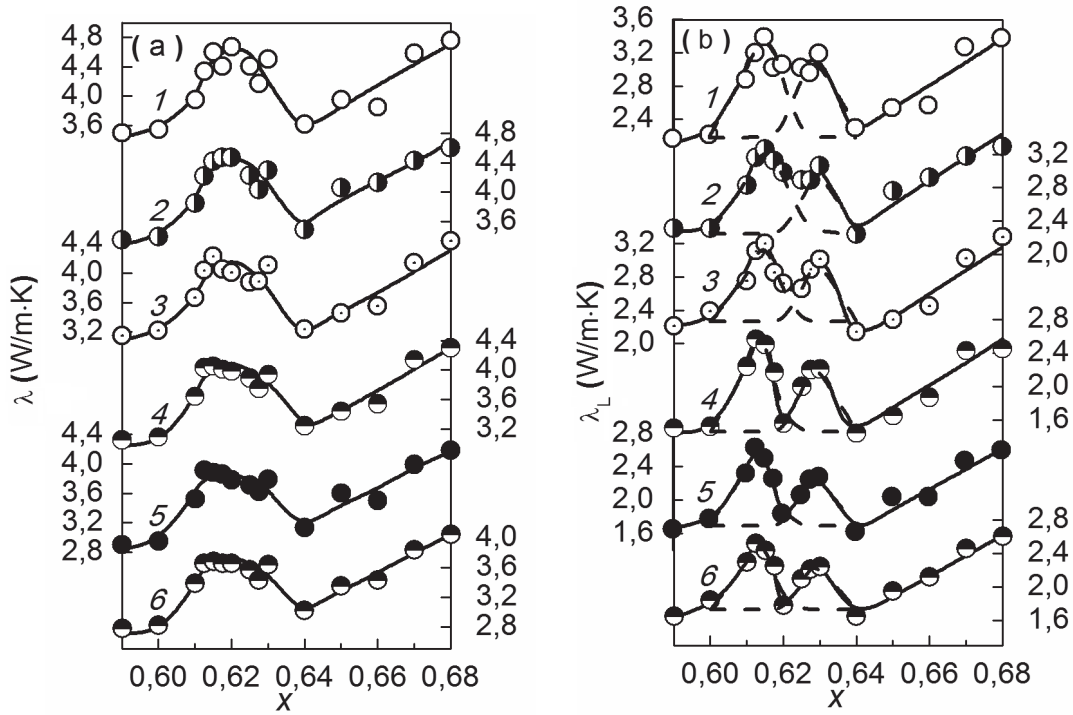

Fig. 1. The dependences of the total λ (a) and lattice λ_L (b) thermal conductivities on composition of the $Pb_{1-x}Sn_xTe$ solid solutions in the vicinity of inversion point at the different temperatures: *1* — 170 K, *2* — 200 K, *3* — 220 K, *4* — 250 K, *5* — 270 K, *6* — 300 K.

mirror symmetry metallic electronic states appear on the semiconductor surface due to the band inversion. In other words, one can assume that the band inversion stimulates a structural rearrangement, at least a local one (long-range or short-range ordering, formation of complexes), and leads to the emergence of the conditions necessary for the formation of a surface layer with TCI properties. However, one should not exclude an alternative mechanism of the TCI transition. It is possible that a necessary condition for the occurrence of the TCI transition is a preliminary structural reorganization, stimulated by a strong electron-phonon interaction, which leads to the band inversion and the formation of a topological layer with its unique properties. The probability of such structural rearrangement can be higher for certain optimal compositions.

Taking into account a strong electron-phonon interaction in the $Pb_{1-x}Sn_xTe$ alloys, as well as the presence of the two peaks in the $\lambda_e(x)$ dependences, we can conclude that both processes — rearrangements in the electronic and lattice subsystems of the crystal — should occur upon reaching approximately the same composition. However, for the realization of one of these processes, some excess of tin in the crystal lattice is required. To reveal the nature of possible structural rearrangement during the TCI transition, detailed structural studies of alloys with compositions near the critical one at various fixed temperatures are needed.

The assumption about a possible change in the local symmetry of atoms and electron structure in the concentration interval near the critical composition is consistent with the conclusions of the authors of [12] based on Mossbauer spectroscopy studies about the $Pb_{1-x}Sn_xTe$ phonon spectrum softening leading to the reduction in the symmetry of the Sn atom environment in a gapless state. However, the conclusions made in [12] were not confirmed in [13] where the authors also used the Mossbauer spectroscopy method. At the same time, the minimum of microhardness observed in [6] in the $Pb_{1-x}Sn_xTe$system in the vicinity of the critical composition x_c, indicated a reduction in the level of strain in the crystal lattice and led to the suggestion about self-organization processes occurring in the system when it approaches the critical composition. A similar decrease in microhardness was also observed in the $Bi_{1-x}Sb_x$ solid solutions during the transition to a gapless state, accompanied by the band inversion [14]. Although both the

crystal and band structures of the $Pb_{1-x}Sn_xTe$ and $Bi_{1-x}Sb_x$ solid solutions are different, both systems are characterized by a strong electron-phonon interaction.

Let us note that the results of theoretical calculations reported by some authors support the idea about a possible structural rearrangement near the topological transition. In a few theoretical studies of the $Pb_{1-x}Sn_xTe$ band-gap evolution under changing x, it was mentioned that when calculating the critical composition x_c, one should take into consideration the disorder in the crystalline structure inherent to substitutional alloys. The authors of [15] carried out ab initio electronic structure calculations within the generalized gradient approximation taking into account the local disorder and showed that the theoretically calculated dependence of band gap on composition is in good agreement with experimental results. In [16], the authors took into account the local disorder in the $Pb_{1-x}Sn_xTe$ solid solutions and concluded that a sharp transition between a trivial and nontrivial topology of the alloy band structure at low temperatures exists in the virtual crystal approximation only, while for more realistic models of crystals the transitions are diffuse. However, there is no experimental confirmation of this prediction so far. Assuming some degree of disorder in substitutional alloys, the authors [17] applied the kernel polynomial method using a tight-binding approach that captures long-range correlations, to determine the critical concentration x_c of $Pb_{1-x}Sn_xTe$, and found that their estimate is in good agreement with the most experimental data. It follows from the theoretical considerations [15–17] that the disorder in the lattice subsystem of the crystal influences the electronic spectrum of the crystal, and the formation of a TCI layer may require certain structural changes in the crystal, which will be manifested in the lattice properties. In other words, we can assume that the band inversion and/or the transition to the TCI state are accompanied by structural changes in the crystal lattice.

Let us also note that in almost all available works, the TCI transition in $Pb_{1-x}Sn_xTe$ was studied at low temperatures, when the critical concentration x_c is in the range $x = 0.25–0.35$. At the same time, the value of x_c strongly depends on temperature, because the temperature coefficients of change in the band gap of PbTe and SnTe have opposite signs and close absolute values. With increasing temperature, the inversion point shifts to higher concentrations x, and near room temperature approaches $x \sim 0.6$ [4, 5]. As temperature increases, the contribution of the phonon subsystem to total energy of the crystal increases and, accordingly, the contribution of the electron-phonon interaction and the probability of a structural rearrangement in the lattice near the inversion point increase. It is possible that at higher temperatures it is easier to observe the complex nature of the transition to a TCI state due to changes in the lattice subsystem of the crystal.

The presence of the lattice instability, which leads to a sharp change in λ_L in a certain concentration range, should be taken into account in the practical use of these and other materials, as well as when predicting and interpreting the properties of the topological layer.

4. Conclusions

It is shown that the TCI phase transition occurring in the $Pb_{1-x}Sn_xTe$ solid solutions is accompanied by anomalies in the properties related not only to electronic but also to the lattice subsystem of the crystal.

In the isotherms (170–300 K) of the lattice thermal conductivity $\lambda_L(x)$, in the vicinity of x corresponding to the transition from a trivial semiconductor to a topological crystalline insulator, we observed two closely spaced peaks near $x = 0.61$ and $x = 0.63$. We suggest that one peak corresponds to the band inversion at the L_6 point of the Brillouin zone. We attribute the other peak to the processes of structural rearrangement (e.g., short ordering) leading to the realization of the TCI transition.

Thus, the method used in this work for studying the TCI phase transition not only makes it possible to accurately determine the critical composition corresponding to the TCI transition at a fixed temperature in a simple way, but also demonstrates the complex nature of such a transition.

The results obtained in this work can be useful for more accurate interpretation of experimental data on TCI transitions. In particular one should take into account the changes in the lattice subsystem of crystal that accompany a TCI transition.

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