Heat capacity and microhardness of the topological crystalline insulator Pb$_{1-x}$Sn$_x$Te near the band inversion composition

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Abstract. The goal of the present work is to reveal effects accompanying the band inversion in Pb$_{1-x}$Sn$_x$Te solid solutions by measuring heat capacity and microhardness. The objects of the study are Pb$_{1-x}$Sn$_x$Te alloys with Sn concentrations in the range of $x = (0.59 – 0.68)$, near the composition corresponding to the transition to a gapless state close to room temperature. It was established that in the Pb$_{1-x}$Sn$_x$Te solid solutions, the transition to the bulk gapless state with the band inversion is manifested through the appearance of peaks in the dependences of specific heat and microhardness on composition at a fixed temperature.

1. Introduction
Narrow band gap semiconductor Pb$_{1-x}$Sn$_x$Te solid solutions are materials widely used in IR - optoelectronics, thermoelectricity and other fields of science and technology [1-3]. The valence band in both SnTe and PbTe consists of two subbands: a non-parabolic light-hole band and a parabolic heavy-hole band. A peculiar feature of the energy band structure of Pb$_{1-x}$Sn$_x$Te alloys is the inversion of the conduction and valence bands which occurs at the certain concentration $x$ and the realization of so-called gapless state (GLS) with zero band gap [3-7]. With increasing temperature, the band gap of Pb$_{1-x}$Sn$_x$Te increases, the distance between light-hole and heavy-hole subbands in the valence band decreases and the position of the GLS point is shifted to higher concentrations of Sn. If the Sn concentration increases at a fixed temperature, the band gap decreases, then at a certain Sn concentration the GLS occurs, and the distance between the light-hole and heavy-hole subbands starts to grow.

Theoretical and practical interest in studying the Pb$_{1-x}$Sn$_x$Te solid solutions has grown sharply in recent years after the prediction and subsequent experimental confirmation of the fact that those solid solutions exhibit properties of topological crystalline insulators (TCIs) in which metallic surface states are protected by the mirror symmetry of the crystal structure [8-10]. Similar to 3D-topological insulators, in the TCIs, the Dirac-cone surface states are produced by bulk band inversion caused by a strong spin-orbit coupling. A topological quantum phase transition between the TCI and trivial phases detected in the Pb$_{1-x}$Sn$_x$Te solid solutions using angle-resolved photoemission spectroscopy was close to the band inversion point in the Pb$_{1-x}$Sn$_x$Te energy band diagram [8-10]. This fact stimulates interest in studying the properties of the Pb$_{1-x}$Sn$_x$Te solid solutions near the composition corresponding to the bulk band inversion in detail.

It can be expected that in the vicinity of the GLS, anomalies in the concentration dependences of both electronic and lattice properties will be observed. By now very few results of detailed experimental studies of electronic properties near the GLS have been reported, and, to the best of our knowledge, there are no data on thermal conductivity, heat capacity, and microhardness in the vicinity of the GLS. Some authors [11-14] tried to detect changes in the local symmetry of atoms and the electron structure in the concentration interval corresponding to the GLS. In [11,12], Pb$_{1-x}$Sn$_x$Te solid solutions ($0<\chi<1$) were studied by Mössbauer's spectroscopy using $^{119}$Sn isotope with a view to
observing changes in the phonon spectrum accompanying a change in the electron spectrum resulting from a strong electron-phonon interaction near the GLS. The authors detected minima in the dependences of quadrupole splitting, isomer shift and Mössbauer's coefficient on the Pb1-xSnxTe solid solution composition in the vicinity of the GLS. They attributed the presence of the concentration-dependent anomalies [11,12] to a decrease in the frequency of optical phonons, or, in other words, the Pb1-xSnxTe phonon spectrum softening, and, as a result, a reduction in the symmetry of the Sn atom environment and strengthening of the electron-phonon interaction in the GLS.

However, the authors of [13] pointed out some experimental imperfections of the studies carried out in [11,12] and conducted a similar study of Pb1-xSnxTe solid solutions (0<x<1) by absorptive Mössbauer's spectroscopy using 119Sn and 129mTe(129T) isotopes in order to detect possible changes in the local symmetry and electron structure of cation and anion nodes, as well as the intensity of the electron-phonon interaction near the GLS. According to the results reported in [13], in the vicinity of the GLS in Pb1-xSnxTe solid solutions, no anomalous changes in the Mössbauer's spectra width both at 80K and at 295K and no anomalous changes in the electron structure of atoms in the cation and anion sublattices are observed. That is why it was concluded in [13] that Mössbauer's spectroscopy with 119Sn and 129mTe(129T) isotopes does not reveal any changes either in the local symmetry of nodes or in the electron structure of atoms or in the intensity of the electron-phonon interaction in the Pb1-xSnxTe solid solutions near the GLS. The same results were obtained later in [14] for 65Cu and 67Ga isotopes at 80K.

The goal of the present work was to investigate the behavior of the concentration dependences of specific heat $C_p$ and microhardness $H$ in the vicinity of the band inversion point in the Pb1-xSnxTe solid solutions. The objects of the study were Pb1-xSnxTe alloys with x in the range of $x = (0.59 – 0.68)$, near the composition corresponding to the transition to the GLS close to room temperature.

2. Experimental
Polycrystalline samples of Pb1-xSnxTe solid solutions were synthesized from high-purity elements in evacuated quartz ampoules and annealed for 300 h at 820 K. All samples exhibited p-type conductivity. The measurements of $C_p(T)$ were performed on the samples prepared by hot pressing from the polycrystalline bulks and subsequent annealing at 820 K during 200 h. The specimens for measuring $C_p$ were prepared in the form of cylinders 15 mm in diameter and 10 mm long. For all samples, the heat capacity was measured in the range of $170 – 570$ K using an adiabatic calorimeter apparatus IT-C-400 in the regime of dynamic heating. For each sample, at least four $C_p$ measurements were taken and their results were averaged. The variation in the thus-obtained $C_p$ values for each sample did not exceed 2%. On the basis of the measured $C_p(T)$ dependences, the $C_p(T)$ isotherms were plotted.

The microhardness $H$ was measured using a PMT-3 apparatus with a pyramidal diamond indenter at a load of 0.49 N. The H values were obtained as the mean value of the measurement of 30 indentations, the relative standard error being 0.5 - 1%.

3. Results and Discussion
In figure 1a, the temperature dependences of $C_p$ for several Pb1-xSnxTe samples are presented. For the rest of the prepared samples, the character of the $C_p(T)$ dependences was similar. It is seen that all the $C_p(T)$ dependences have a minimum near 400 K. The presence of the minimum distinguishes the $C_p(T)$ dependences for the Pb1-xSnxTe solid solutions in the vicinity of the GLS from those for the constituents PbTe and SnTe, for which the lattice specific heat remains practically constant above the Debye temperature. To all appearances, such behavior of the $C_p(T)$ dependences is connected with the specificity of the GLS and requires more detailed studies for the correct interpretation of the experimental results.

On the basis of the temperature dependence of $C_p$, we plotted specific heat isotherms, which are presented in figure 1b. As is seen, there is the pronounced peak in the $C_p$-isotherms near the composition $x = 0.62$, corresponding to the transition into the GLS near room temperature [1]. That is
why the observed anomaly in the $C_p$ concentration dependences can be viewed as a critical phenomenon accompanying a second-order phase transition connected with the transition into the GLS with band inversion.

The minimum in microhardness (figure 1c), which is also observed at the critical composition, indicates a reduction in the level of strain in the crystal lattice and leads to a suggestion about self-organization processes occurring in the system when it approaches the critical composition.

**Figure 1.** The temperature dependences of the specific heat $C_p$ (a), the isotherms of $C_p$ (b), and room-temperature dependence of the microhardness $H$ (c) on the Pb$_{1-x}$Sn$_x$Te solid solution composition $x$. a: 1 - $x = 0.6225$; 2 - $x = 0.6$; 3 - $x = 0.68$

The data obtained in this work show that, under the transition into the GLS, a change in the local symmetry of atoms and electron structure in the concentration interval corresponding to the GLS occurs with a high probability which is consistent with the conclusions of the authors of [11,12] about the Pb$_{1-x}$Sn$_x$Te phonon spectrum softening leading to the reduction in the symmetry of the Sn atom environment and intensified electron-phonon interaction in the GLS.
4. Conclusions
It was established that in the temperature interval 170-570 K, the temperature dependences of the specific heat $C_p$ of the Pb$_{1-x}$Sn$_x$Te solid solutions with $x$ close to the concentration corresponding to the transition into the GLS, represent curves with a minimum.

It was shown that in the Pb$_{1-x}$Sn$_x$Te solid solutions, the transition to the bulk gapless state with the band inversion which is accompanied by the topological quantum phase transition from a TCI phase to a trivial phase [8-10] is manifested through the appearance of peaks in the dependences of specific heat and microhardness on composition at a fixed temperature.

It is suggested that the transition into the GLS is a second-order phase transition, which is accompanied by changes not only in the electron but also in the phonon spectrum and, with a high probability, by ordering processes.

Acknowledgement
This work was supported by the Ukrainian Ministry of Education and Science (Project # M3925).

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