

Temperature and concentration dependences of specific heat of $\text{Bi}_{1-x}\text{Sb}_x$ solid solutions

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For $\text{Bi}_{1-x}\text{Sb}_x$ solid solutions, the concentration ($x = 0 - 0.12$) and temperature (170–525 K) dependences of specific heat C_p were obtained. At all temperatures studied, three peaks of C_p were observed near $x = 0.015$, $x = 0.037$, and $x = 0.07$. The observed effects were attributed to critical phenomena accompanying the second-order phase transitions: percolation transition from dilute to concentrated solid solutions, the transition to a gapless state, and the semimetal-semiconductor transition, respectively. It was shown that the values of critical indexes ($\alpha = 0.11 \pm 0.01$) are the same not only for different peaks but also for different temperatures and correspond to the values theoretically calculated within the framework of scale-invariant theory for three-dimensional (3D) models.

Keywords: $\text{Bi}_{1-x}\text{Sb}_x$ solid solutions, composition, temperature, specific heat, phase transition.

Для твердых растворов $\text{Bi}_{1-x}\text{Sb}_x$ получены концентрационные ($x = 0 - 0.12$) и температурные (170–525 K) зависимости удельной теплоемкости C_p . При всех исследованных температурах наблюдались три пика C_p вблизи $x = 0.015$, $x = 0.037$ и $x = 0.07$. Это связывается с критическими явлениями, сопровождающими фазовые переходы второго рода: переход перколяционного типа от разбавленных к концентрированным твердым растворам, переход в бесщелевое состояние и переход полуметалл — полупроводник, соответственно. Показано, что значения критических индексов ($\alpha = 0.11 \pm 0.01$) одинаковы не только для различных пиков, но и для различных температур и соответствуют значениям, теоретически рассчитанным в рамках масштабной-инвариантной теории для трехмерных (3D) моделей.

Температурні та концентраційні залежності питомої теплоємності $\text{Bi}_{1-x}\text{Sb}_x$ твердих розчинів. *О.І.Рогачова, Г.М.Дорошенко, О.М.Нащекіна.*

Для твердих розчинів $\text{Bi}_{1-x}\text{Sb}_x$ одержано концентраційні ($x = 0 - 0.12$) та температурні (170–525 K) залежності питомої теплоємності C_p . При всіх температурах, що досліджувалися поблизу $x = 0.015$, $x = 0.037$ та $x = 0.07$ спостерігаються піки C_p . Це пов'язується із критичними явищами, які супроводжують переходи другого роду: перколяційний перехід від розведених до концентрованих твердих розчинів, перехід у безщільний стан і перехід напівметал-напівпровідник відповідно. Показано, що значення критичних індексів ($\alpha = 0.11 \pm 0.01$) однакові не тільки для різних піків, але також для різних температур і відповідають значенням, які теоретично розраховані у межах масштабної-інваріантної теорії для тривимірної (3D) моделі.

1. Introduction

The $\text{Bi}_{1-x}\text{Sb}_x$ solid solutions between Bi and Sb semimetals are well known as promising thermoelectric and thermomagnetic

materials for cooling devices of various types, most effectively used at the temperatures below 150–200 K [1, 2]. In addition, in view of the fact that Bi and Sb form a continuous series of solid solutions, they

are very convenient objects of solid state physics for studying the effect of a continuous change in composition on both the electronic and lattice subsystems of a crystal. In particular, one can expect that when composition is changed in such a wide range of concentrations, concentration phase transitions (PTs) might take place lead to a radical change in the properties of the system. Interest in physical properties of the $\text{Bi}_{1-x}\text{Sb}_x$ solid solutions has increased dramatically after it was found out that the $\text{Bi}_{0.9}\text{Sb}_{0.1}$ solid solution is a 3D topological insulator [3, 4] and that the best thermoelectric materials are the topological insulators [5].

Bi and Sb have the similar types of chemical bond and layer-like crystal structure (arsenic type) [6]. It is known by now that under changing composition, the band structure of $\text{Bi}_{1-x}\text{Sb}_x$ changes in a complex way [7, 8], passing through a number of specific electronic states. These changes affect the behavior of electronic properties. Bismuth is a semimetal with two (T and L_s) valence bands with different effective masses. The T-band overlaps with the L_α -conduction band at the T-point of the Brillouin zone, determining semimetallic properties of Bi. The L_s valence band is separated from the L_α conduction band at the L-point by a small gap. With increasing Sb content, the energy distance between the L_α and L_s bands decreases, and at $x = 0.02$ – 0.04 (different authors report different concentrations) a gapless state is realized and band inversion occurs. The maximum values of the thermomagnetic efficiency at ~ 140 K are attained in solid solutions in the semimetallic region ($x \sim 0.03$ – 0.04), which are widely applied in Etingshausen refrigerators. As x increases further, the energy distance between the L_α and L_s bands starts to increase again. On the other hand, with increasing x , the T-valence band decreases in energy, and its overlap with bands at the L and T points vanishes at $0.06 \leq x \leq 0.07$, resulting in the semimetal-semiconductor transition. When the T-valence band drops below the L-valence band (at $x \sim 0.085$ – 0.09), the system becomes a direct gap semiconductor with small effective mass Dirac-like bands. In the range of $x = 0.07$ – 0.22 , the $\text{Bi}_{1-x}\text{Sb}_x$ solid solutions exhibit semiconducting properties, and the highest value of thermoelectric figure of merit $Z = (S^2\sigma)/\lambda$ (S is the Seebeck coefficient, σ is the electrical conductivity, and λ is the thermal conductivity) is observed at $x = 0.12$ – 0.14 [1, 2].

Earlier [9–12], for $\text{Bi}_{1-x}\text{Sb}_x$ solid solutions ($x = 0$ – 0.12) at room temperature we observed the anomalies in the concentration dependences of σ , S , λ , Hall coefficient R_H , charge carrier mobility μ and magnetoresistance $\Delta\rho/\rho$ near $x \sim 0.01$, ~ 0.03 and ~ 0.07 . We attributed those peculiarities to critical phenomena accompanying electronic second-order PTs, specifically, the transition of a percolation type from the dilute to concentrated solid solution, the transition to a gapless state accompanied by the L-point inversion, and the semimetal – semiconductor transition, respectively. It was shown [13] that these transitions are accompanied by structural changes in the crystal lattice, which indicates a strong electron-phonon interaction in $\text{Bi}_{1-x}\text{Sb}_x$ solid solutions. In [14], we showed that the observed anomalies in the room-temperature concentration dependences of kinetic properties correspond to the anomalies in the concentration dependences of specific heat C_p and that the experimentally determined values of the critical exponents α for the C_p peaks ($\alpha \sim 0.11$) are in good agreement with the values theoretically calculated within the framework of scale-invariant theory. The question arises whether C_p peaks will be observed at other temperatures and whether α values will depend on temperature. Although the temperature dependences of C_p for bismuth have been studied in a number of works [15–21], the number of studies of the $C_p(T)$ dependences for $\text{Bi}_{1-x}\text{Sb}_x$ solid solutions is very limited. Such dependences were obtained either for selected compositions of $\text{Bi}_{1-x}\text{Sb}_x$, or for a series of compositions but with an increment in concentration of at least $\Delta x = 0.1$ [22–24].

The goal of the present work was to measure of C_p temperature dependences for the $\text{Bi}_{1-x}\text{Sb}_x$ solid solutions in the composition range $x = 0$ – 0.12 , to plot isotherms of C_p and to study the effect of temperature on the manifestation of the PTs and critical behavior under the percolation transition and the transition into gapless state. In addition, we intended to find out whether the temperature affects the position of the critical points in the isotherms of electronic properties.

2. Experimental

$\text{Bi}_{1-x}\text{Sb}_x$ samples for measuring C_p were synthesized by a fusion of high-purity (99.999 %) Bi and Sb in the evacuated quartz ampoules at the temperature (980 ± 10) K during 5 h applying vibrational

stirring. The samples were then annealed for 720 h at 520 K and cooled in air. The compositions of the synthesized samples were varied within the concentration range $x = 0-0.12$ with a step of $\Delta x = 0.0025-0.01$. All samples were prepared not only by the same method, but also simultaneously, in the same technological cycle, to exclude any effects related to the slightest differences in technological conditions. The samples for measuring C_p were cylinder-shaped with a diameter of 15 mm and height of 10 mm and were prepared by cold pressing of the powders with the dispersion degree of $\sim 40 \mu\text{m}$ under the pressure of 400 MPa. After pressing, the samples were exposed to the homogenizing annealing for 200 h at 520 K. The average grain size in the samples after cold pressing was $d \approx 40 \mu\text{m}$, and after subsequent annealing for 200 h, d increased up to $d \approx 60 \mu\text{m}$. The porosity did not exceed $\pm 3 \%$. The chemical composition and homogeneity of the samples were controlled using electronic microprobe analysis. Specific heat measurement was carried out in the temperature range 170–525 K on an IT C-400 setup using a comparative method of the dynamic C-calorimeter. For each sample, not less than 3–4 measurements of the $C_p(T)$ temperature dependences were performed and the obtained results were averaged. The variation in the C_p data for each sample did not exceed 2%. It is seen from Fig. 1 that the difference between the $C_p(T)$ dependences obtained in this work and those obtained by other authors [15–21] for Bi crystals was within the range of the measurement error.

3. Results and discussion

In Fig. 2, the temperature dependences of the specific heat C_p of some $\text{Bi}_{1-x}\text{Sb}_x$ solid solutions are presented. It is seen that in the investigated temperature range, C_p increases with temperature monotonically, which is consistent with the results of other authors [22–24]. Since Bi and Sb semimetals are characterized by a small overlap of the bands [7, 8] and hence by a small density of states on the Fermi surface, the contribution of the electronic component of specific heat to the total specific heat is considerably smaller than that of ordinary metals and can be neglected at sufficiently high temperatures. The increase in C_p with increasing temperature at temperatures significantly higher than the Debye temperature ($\theta_D^{\text{Bi}} = 120 \text{ K}$ [6, 15] and $\theta_D^{\text{Sb}} =$

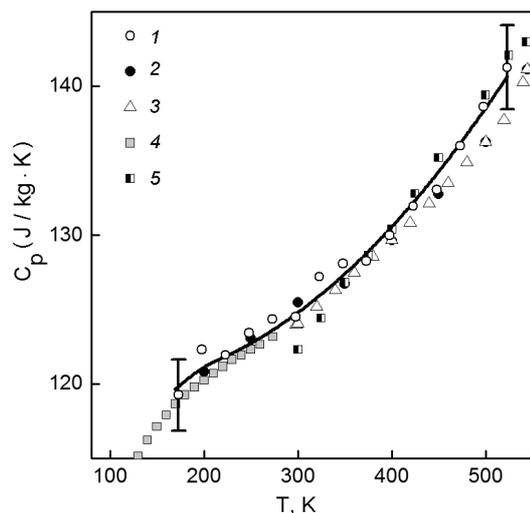


Fig. 1. Temperature dependences of the bismuth specific heat C_p according to the data of various authors: 1 — this work; 2 — [21]; 3 — [19]; 4 — [18]; 5 — [17].

210 K [6, 16]) may indicate the presence of anharmonic effects and/or formation of vacancies in crystal upon its heating. The anharmonic additive can be associated with structural features, as well as with the expansion of metals with increasing temperature. The authors of [16, 17] consider that the increase in C_p under heating is mainly due to the significant role of the anharmonic effects for layered crystals, and the authors of [19] attribute this increase in C_p to the contribution of point defects (vacancies). The anharmonic component of C_p of Bi and Sb, along with other contributions, was calculated in [21], and the authors concluded that the excess lattice heat capacity at high temperatures is mainly due to anharmonic effects, rather than formation of vacancies.

Based on the temperature dependences $C_p(T)$, the C_p isotherms were plotted. In Fig. 3a, some of those isotherms (at 200, 300, 400, and 550 K) are shown. In the isotherms, three peaks are clearly seen near compositions $x = 0.015$, 0.037 and 0.07. One can also see that in the isotherms corresponding to temperatures both higher and lower than room temperature, the positions of the peaks and their height do not practically change. For all isotherms, the general tendency to increase in C_p under increasing Sb concentration is observed. The concentration dependence of C_p which would be in the case of an additive $C_p(x)$ dependence is shown by the dotted line.

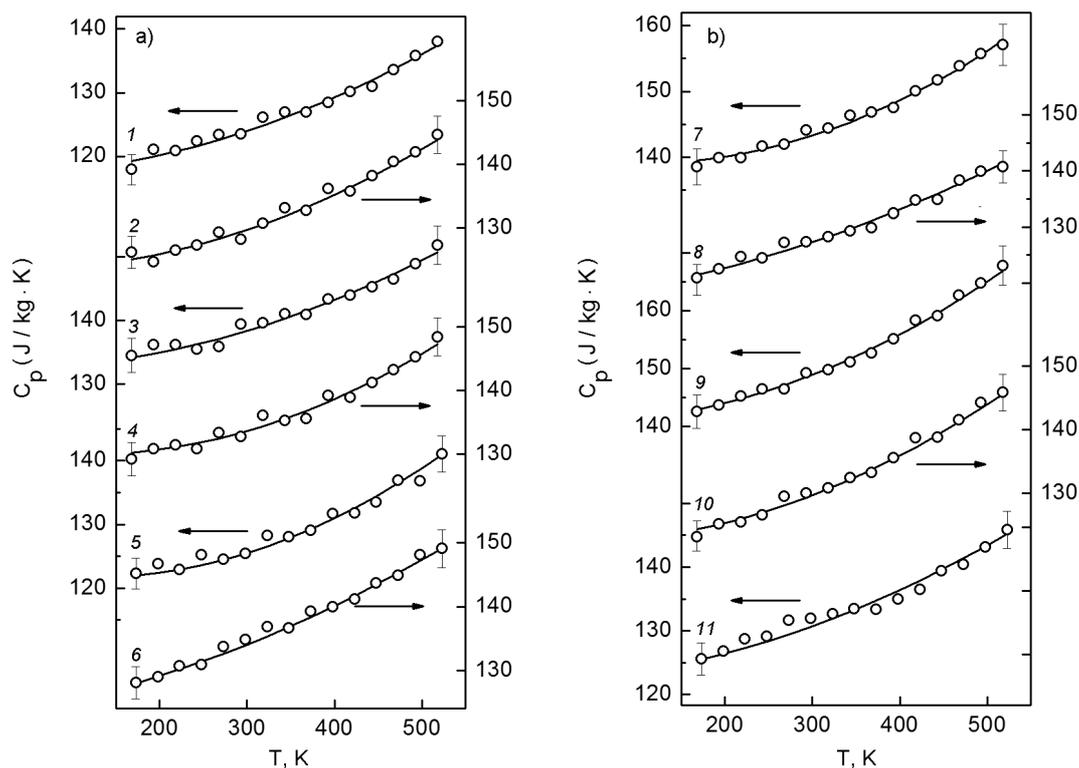


Fig. 2. Temperature dependences of the $\text{Bi}_{1-x}\text{Sb}_x$ specific heat C_p : $x = 0$ (1); 0.0075 (2); 0.0125 (3); 0.02 (4); 0.025 (5); 0.03 (6); 0.0375 (7); 0.055 (8); 0.07 (9); 0.09 (10); 0.12 (11).

For the quantitative description of the C_p critical behavior near the peaks, we isolated the anomalous part of the specific heat ΔC_p . In Fig. 3b, the excess specific heat obtained by subtracting the peak contributions from the background value of C_p , which was estimated using the additive line in Fig. 3a is presented.

The presence of a λ -peak in the temperature or concentration dependences of specific heat is one of the typical characteristics of second-order PTs. According to the fluctuation theory of second-order PTs, near PT, properties are determined by strongly interacting fluctuations, the correlation radius of which sharply increases when approaching the point of the PT and becomes infinite at the PT point. In the vicinity of the PT, the properties change according to a power law and the system becomes nonlinear [25–31].

The distinct peaks in C_p isotherms indicate the presence of concentration-dependent PTs in the $\text{Bi}_{1-x}\text{Sb}_x$ solid solutions not only at room temperature, but also in the entire temperature interval studied. Just as in [14], the critical indices were determined only for the first and second peaks. For the third peak, the critical indices cannot be accurately determined because of the small

number of experimental points in the immediate vicinity of that peak.

To determine the C critical indexes for each of the isotherms, we used the basic concepts of the fluctuation theory of second-order PTs and critical phenomena based on the hypothesis of scale similarity of fluctuations [25–31], as well as the analogy between temperature- and concentration-dependent second-order PTs. Based on that, the critical behavior of the excess specific heat ΔC_p near the critical concentration x_c can be described by the following equation:

$$\Delta = A^\pm |\eta|^{-\alpha}, \quad (1)$$

where $\eta = (x - x_c)/x_c$ is the reduced concentration, α is the specific heat critical index, and A^\pm is the specific heat critical amplitude. The "plus" and "minus" signs refer to the cases where $x < x_c$ and $x > x_c$, respectively. Critical indexes describe the behavior of physical quantities near the second-order PTs. It is believed that they are universal, i.e. they do not depend on the details of the physical system, but only on the dimension of the system, the range of the interaction, and the spin dimension [25–31].

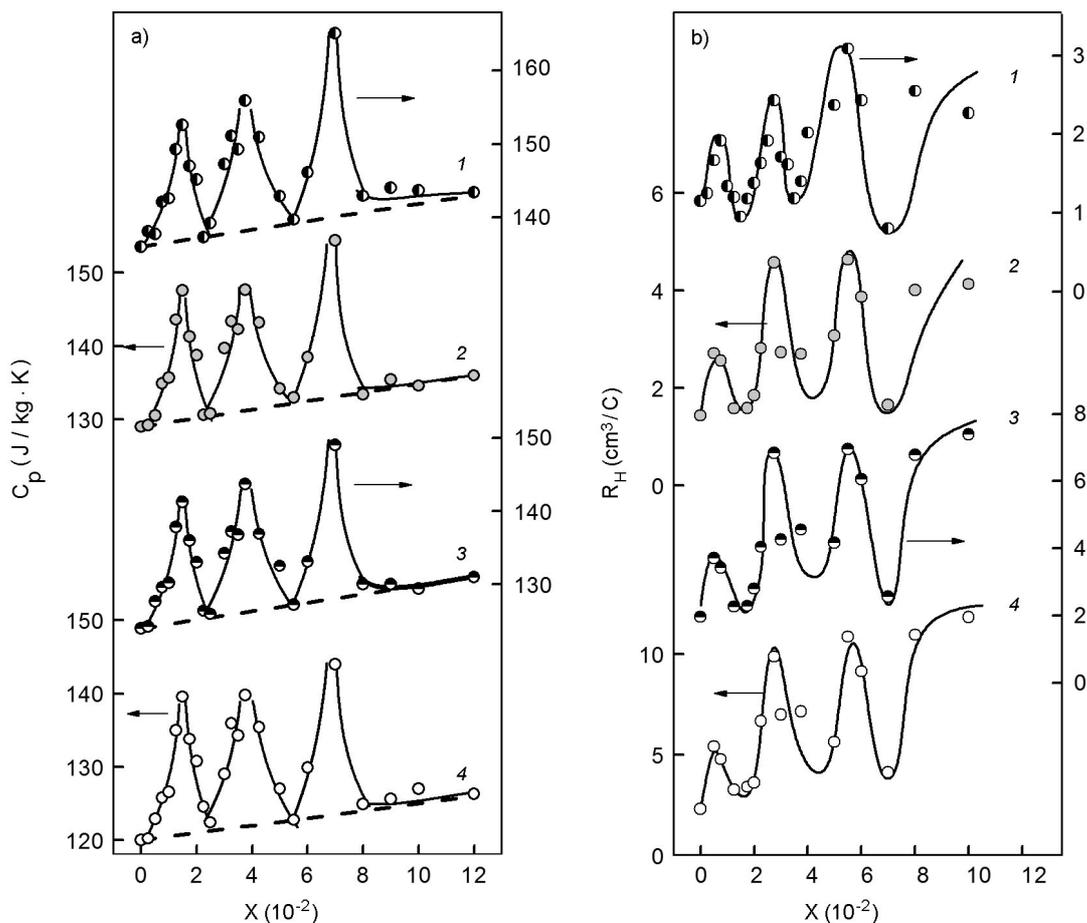


Fig. 3. The dependences of the specific heat C_p (a) and the Hall coefficient R_H (b) on the composition x of the $\text{Bi}_{1-x}\text{Sb}_x$ solid solutions at the different temperatures: C_p : 500 K (1); 400 K (2); 300 K (3); 200 K (4). R_H : 300 K (1); 250 K (2); 200 K (3); 150 K (4). The dotted line in the Fig. 3(a) corresponds to the law of additivity.

It is known that in the study of critical properties, the correct determination of the critical temperature T_C or concentration x_C is important, since most often T_C or x_C do not exactly coincide with the maximum of the heat capacity and other properties. Therefore when determining values of x_C and α , one of the assumptions of the static scaling hypothesis about the equality of the critical indexes α measured above and below the x_C value was used for temperatures below and above room temperature in the interval 170–525 K. Using this assumption and applying the least square method, we found the average values of x_C , α and A^+/A^- for isotherms in the investigated temperature range (Table 1).

A more accurate description of the experimental results is possible when approximating the critical behavior of the specific

Table 1. The values of the $\text{Bi}_{1-x}\text{Sb}_x$ critical parameters obtained in the numerical calculation of the critical behavior of the specific heat at different temperatures using Eq. (1)

T, K	$x_C \cdot 10^2$	α	A^+/A^-
200	1.500±0.005	0.110±0.005	1.38 ^
300	1.500±0.005	0.110±0.005	1.35 ^
400	1.500±0.005	0.115±0.005	1.28 ^
500	1.500±0.005	0.115±0.005	1.22 ^

heat by an expression taking into account the corrections to scaling [25–31]:

$$\Delta C_p = A^\pm |\eta|^{-\alpha} (1 + D^\pm |\eta|^{\Delta-\alpha}), \quad (2)$$

where coefficients D^\pm and Δ are the correction coefficients to the asymptotic behavior of the specific heat near the critical point:

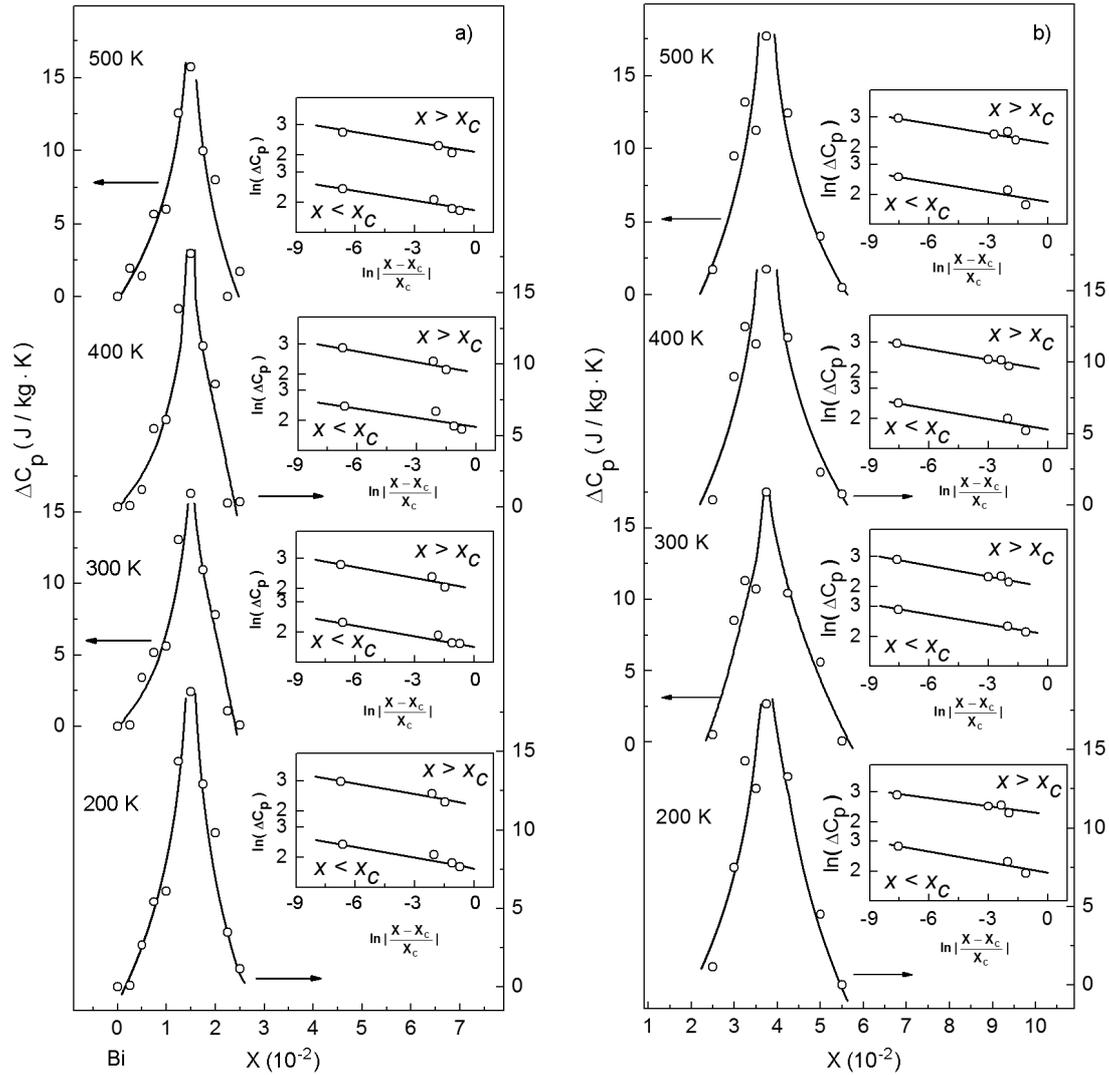


Fig. 4. The excess specific heat ΔC_p of the $\text{Bi}_{1-x}\text{Sb}_x$ solid solutions versus the composition x at 200, 300, 400 and 500 K near the first peak at $x = 0.015$ (a) and the second peak at $x = 0.037$ (b). Insets: Approximation of the ΔC_p versus the reduced concentration $\eta = (x - x_c)/x_c$ dependence at $x < x_c$ and $x > x_c$ by the linear function using a double logarithmic scale.

D^\pm is the amplitude of the correction to the scaling (scale invariance), Δ is the correction index for scaling ($\Delta = 0.55$). Using this assumption and applying the least square method, we found the average values of x_c , α , A^+/A^- and D^+/D^- for isotherms in the investigated temperature range (Table 2). Based on the thus obtained values of x_c , α , A^+/A^- and D^+/D^- , the $\Delta C_p(x)$ dependences were plotted in double logarithmic coordinates, which are consistent with the experimental data and describe the critical behavior of C_p near the PT in the range of $\eta = (2-5) \cdot 10^{-1}$ rather accurately (Fig. 4). As can be seen from Fig. 4,

Table 2. The average values of the $\text{Bi}_{1-x}\text{Sb}_x$ critical parameters obtained in the numerical calculation of the critical behavior of the specific heat at different temperatures using Eq. (2).

$x_c \cdot 10^2$	α	A^+/A^-	D^+/D^-
1.50 ± 0.005	0.11 ± 0.01	1.20	1.11
3.75 ± 0.005	0.11 ± 0.01	1.02	0.93

using the theoretical value of the critical specific heat index $\alpha = 0.11 \pm 0.01$, expression (2) approximates the behavior of ΔC_p near the maxima rather well.

The determined values of x_C and α for the first and second peaks, within the error of their determination, corresponded to the same values for room temperature [14]. The positions of the peaks also did not differ from those at room temperature. Besides, the obtained values of the specific heat critical exponents α are close to those determined experimentally for the second-order temperature PTs, taking place in other materials [26–36]. Those values are also in good agreement with the values calculated theoretically for three-dimensional case using different methods [26–36], particularly for the universality class of the classical 3D Heisenberg ferromagnetic.

In order to further confirm the presence of second-order concentration PTs at the concentrations indicated above, the Hall coefficient R_H isotherms were obtained. In Fig. 3b, the isotherms constructed on the basis of the temperature dependences of R_H are presented for some compositions. It can be seen that there is a general tendency for R_H to increase with increasing Sb content, but at the same time three peaks are observed in the $R_H(x)$ dependence at concentrations corresponding to the compositions at which λ -peaks of C are observed. This confirms the existence of critical phenomena that accompany the second-order PTs.

It should be emphasized that the phenomena corresponding to the three peaks in C_p isotherms, as well as the isotherms of various properties, are of different nature. The first peak corresponds, from our point of view [9–14], to the transition of percolation type from dilute to concentrated solid solutions. One can draw an analogy with Mott transition in semiconductors with impurities. With the almost complete absence of thermal excitation of electrons (holes), which is practically realized at very low temperatures, with increasing impurity concentration, electronic shells of individual atoms begin to overlap, at some point a single chain is formed that connects these shells, impurity band conductivity arises, and the metal-dielectric transition takes place. At some point, the impurity band merges with the conduction band. Hence, it is clear that low temperatures and initially low impurity concentrations are needed to detect the Mott transition. One of the models proposed by Mott for describing this dielectric-metal transition is a percolation model, within which an infinite cluster is first formed in the critical point (percolation threshold). The phenomena described

by percolation theory refer to so-called critical phenomena, which are cooperative, since they are caused by the properties of the entire set of particles, and not by the individual properties of each particle. Near the critical point, the system appears to be divided into blocks with different properties, whose size grows indefinitely when approaching the critical point. The consequence of this is the singular character of changes in physical properties near critical points and the universality of the behavior of objects that differ in the microscopic nature of the interaction responsible for the transition. A region of universality appears near the critical points. According to modern concepts [32], percolation transitions are among the second order PTs, which are also accompanied by critical phenomena.

In our case, we have a semimetal in which there is initially a band overlap and high carrier concentrations, so the peak we observed near $x = 0.01$ is not associated with the overlapping of the electron shells but has a different nature. We assume that in this case we deal with short-range deformation interactions. It is confirmed by the presence of anomalies of microhardness near $x \sim 0.01$, which we observed in a large number of solid solutions [37–42].

The second peak, which we observe through the measurement of specific heat in $\text{Bi}_{1-x}\text{Sb}_x$ as Sb concentration increases to $x \sim 0.0375$ (Fig. 3) can be attributed to the transition to an gapless state. Indeed, taking into account a strong electron-phonon interaction in $\text{Bi}_{1-x}\text{Sb}_x$ which becomes comparable with phonon energy as the band gap decreased, one can expect a qualitative change in the electron subsystem state under transition into the gapless state. The significant deviation from Vegard's law and the narrowing of diffraction lines near $x \sim 0.0375$ we observed in [13] indicate structural changes in the same crystal structure. The deviation from Vegard's law near this composition suggests that this electronic transition is accompanied by self-organization processes. As for as the third peak we attribute it to the semimetal-semiconductor transition.

Thus, it follows from the results obtained that all three transitions take place in the entire temperature range studied in this work. One could expect that with increasing temperature, with increasing intensity of thermal motion of atoms, the probability of self-organization processes will decrease and the intensity of the peaks will decrease too. But this is not observed.

4. Conclusions

The temperature dependences ($T = 170\text{--}525$ K) of the $\text{Bi}_{1-x}\text{Sb}_x$ solid solutions specific heat C_p were obtained in the composition range $x = 0\text{--}0.12$, and the isotherms of C_p based on these dependences were plotted.

It was shown that three peaks at $x = 0.015$, $x = 0.0375$ and $x = 0.07$ that had been observed previously in the room-temperature $C_p(x)$ dependences, manifest themselves at all temperatures studied in this work. The position of the peaks in the C_p isotherms, as well as the C_p critical exponents for the first and second peaks calculated using the fluctuation scale-invariance theory of second-order PTs for 3D-systems, practically do not change.

On the basis of the temperature dependences of the Hall coefficient R_H , the isotherms of $R_H RH$ were built. It was established that the positions of peaks in the R_H isotherms correspond to C_p peaks positions and practically do not change with changing temperature. The existence of the peaks in the R_H isotherms confirms the presence of critical phenomena.

Experimental studies confirm the principle of universality and show that the numerical values of the critical exponents within the experimental error correspond to the results of the theory. In the vicinity of the critical point, the fluctuations are so great that the microscopic details of short-range intermolecular interactions turn out to be insignificant

The obtained results represent another confirmation of our previous assumptions that the detected concentration anomalies of the electronic and thermal properties are a manifestation of the critical phenomena accompanying second-order phase transitions, connected with 1) transition of percolation type from dilute to concentrated solid solutions, 2) transition into gapless state and 3) semimetal-semiconductor transition.

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