Specific heat of $Bi_2(Te_{1-x}Se_x)_3$ solid solutions

K.V.Martynova, E.I.Rogacheva, G.V.Lisachuk

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

The temperature dependences of the specific heat C_p in the temperature range $T = 175–500$ K were obtained for $Bi_2(Te_{1-x}Se_x)_3$ solid solutions ($x = 0÷0.06$). The peaks of specific heat are revealed on the isotherms of C_p, the presence of which is attributed to the realization of the percolation-type phase transition from dilute solid solutions to concentrated ones. The obtained value of the critical index for the composition dependences $C_p(x)$ ($\alpha = 0.105$) corresponds to the values of α for specific heat in case of the second-order phase transitions. The results of this work confirm the previously suggested assumption that the concentration anomalies of electrophysical properties observed in the study of $Bi_2(Te_{1-x}Se_x)_3$ solid solutions can be interpreted as the manifestation of the critical phenomena accompanying the percolation-type phase transition from dilute to concentrated solid solutions.

Keywords: $Bi_2(Te_{1-x}Se_x)_3$ solid solution, specific heat, composition, temperature, percolation, critical phenomena, critical index.

Теплоємність твердих розчинів $Bi_2(Te_{1-x}Se_x)_3$. *К.В.Мартинова, О.І.Рогачова, Г.В.Лісачук*

Для твердих розчинів $Bi_2(Te_{1-x}Se_x)_3$ ($x = 0÷0.06$) отримано температурні залежності питомої теплоємності C_p в інтервалі температур $T = 175–500$ К. На ізотермах C_p при складі $x = 0.02$ виявлено піки теплоємності, наявність яких пов'язується з існуванням фазового переходу перколяційного типу від розведених твердих розчинів до концентрованих. Отримане значення стіпеневого коефіцієнта α у концентраційних залежностях $C_p(x)$ ($\alpha = 0.105$) відповідає значенням α для теплоємності у випадку фазових переходів ІІ роду. Результати даної роботи є підтвердженням висловленого раніше припущення про те, що концентраційні аномалії електрофізичних властивостей, які спостерігалися нами при дослідженні твердих розчинів $Bi_2(Te_{1-x}Se_x)_3$, є проявом критичних явищ, що супроводжують фазовий перехід перколяційного типу від розведених до концентрованих твердих розчинів.

Для твердых растворов $Bi_2(Te_{1-x}Se_x)_3$ ($x = 0÷0.06$) получены температурные зависимости удельной теплоемкости C_p в интервале температур $T = 175–500$ К. На изотермах C_p при составе $x = 0.02$ выявлены пики теплоемкости, существование которых связывается с существованием фазового перехода перколяционного типа от разбавленных твердых растворов к концентрированным. Полученное значение степенного коэффициента α в концентрационных зависимостях $C_p(x)$ ($\alpha = 0.105$) соответствует значениям α для теплоемкости в случае фазовых переходов ІІ рода. Результаты данной работы являются подтверждением высказанного ранее предположения о том, что концентрационные аномалии электрофизических свойств, которые мы наблюдали при исследовании твердых растворов $Bi_2(Te_{1-x}Se_x)_3$, являются проявлением критических явлений, которые сопровождают фазовый переход перколяционного типа от разбавленных к концентрированным твердым растворам.

1. Introduction

Materials based on V_2VI_3 are widely used for thermoelectric (TE) cooling close to room temperature [1]. The substitutional $Bi_2(Te_{1-x}Se_x)_3$ solid solutions are currently one of the best materials for use as an *n*-branch of the TE converter [2] which requires a detailed study of the dependences of TE properties on the solid solution composition. In [3, 4] we observed anomalies (an increase in electrical conductivity, decrease in the Seebeck coefficient) of the concentration dependences of the electrophysical and mechanical properties of $Bi_2(Te_{1-x}Se_x)_3$ near x = 0.02, the presence of which was associated with the existence of a percolation-type phase transition (PT) from dilute to concentrated solid solution. Earlier [5, 6] the assumption was made about the universal character of such PT in solid solutions.

The direct way to prove or disprove the existence of a particular PT is the study of specific heat. To date, few works have been devoted to the study of the specific heat of $Bi_2(Te_{1-x}Se_x)_3$ solid solutions. The main thermodynamic characteristics (entropy, enthalpy, reduced Gibbs energy, etc.) of these alloys [7] and Debye temperature for Bi_2Te_3 (Θ_D = 162 K [8]) and Bi_2Se_3 (Θ_D = 105.5 K [9]) were determined. It was shown that the experimentally obtained temperature dependences of C_p for $Bi_2(Te_{1-x}Se_x)_3$ at $T <$ 200 K could be well described in the framework of Debye's theory, taking into account the contribution of electronic specific heat [10]. However, at higher temperatures, the values of C_p, obtained experimentally [9, 11], exceed the theoretical values.

The $C_p(x)$ dependences for x = 0−1 obtained in [7, 9] follow the additivity law, but in these works $C_p(x)$ has a big step on composition (Δx = 0.1) and also there is no information about composition dependence of C_p in the range $x <$ 0.1. Thus, from the available literature data on the specific heat of the $Bi_2(Te_{1-x}Se_x)_3$ system, it is impossible to infer about the presence of a concentration PT in the region of low impurity content. The study of the $C_p(x)$ dependence will confirm or deny the assumption made in [3, 4] about the presence of concentration PT in $Bi_2(Te_{1-x}Se_x)_3$ system at low impurity content.

Therefore, this work was aimed to observe the anomalies of specific heat in $Bi_2(Te_{1-x}Se_x)_3$ solid solution in the x = 0÷0.06 composition range basing on the study of C_p isotherms.
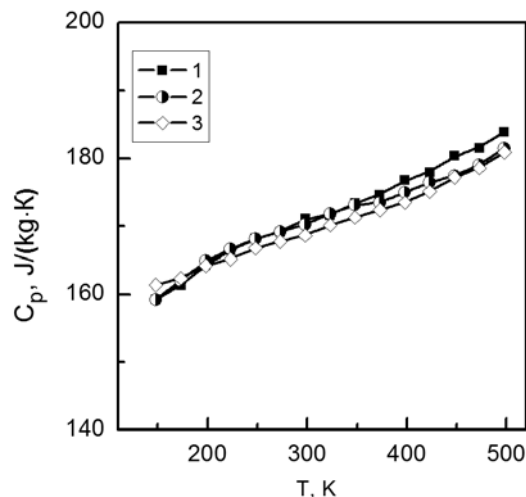

Fig. 1. Experimental temperature dependences of the specific heat C_p for Bi_2Te_3 (curves *1−3* correspond to individual experiments).

2. Experimental

The measurement of C_p was conducted on 20 cold-pressed tablets (d = 15 mm, h = 10 mm) of $Bi_2(Te_{1-x}Se_x)_3$ solid solutions in the range of compositions x = 0÷0.06. Tablets were produced from the cast polycrystals (the sintering method for cast polycrystals is given in [3]). The cast samples were grounded in an automated agate mortar "CBMM", then the powder was sieved (cell size 200 μm). Then the powder was pressed at room temperature on a hydraulic press at a pressure of P = 7t/cm² (holding time t = 1 min). The pressed tablets were annealed in evacuated ampoules of heat-resistant glass at T = 575 K for 200 hours. Specific heat was measured in T = 175−500 K temperature range by the dynamic calorimeter method on the IT-C-400 experimental facility. Before measurements, the surfaces of the samples were sanded to a mirror finish. The thermal contact was provided with KPT-8 thermal paste.

To reduce the measurement error, several measurements of C_p were taken on each sample, and then the average was used. When re-measuring one sample, it was re-installed in the cell, and a layer of thermal paste was reapplied. Fig. 1 shows the results of three measurements of C_p for one sample (Bi_2Te_3) as an example. Statistical processing of experimental data showed that the standard deviation of C_p did not exceed 3 %.

3. Results and discussion

In Fig. 2, the temperature dependences of C_p for samples $Bi_2(Te_{1-x}Se_x)_3$ of different compositions are presented. For all studied samples an increase in C_p with temperature was observed. The growth of C_p above the room temperature was also observed in [9, 11] for bismuth telluride and its solid solutions. The measurement temperatures are significantly higher than Θ_D, and, basing on Debye's theory, we should expect the saturation of $C(T)$ dependence. Therefore, the observed increase in C_p at $T > \Theta_D$ requires further explanation.

Debye's theory is describing the temperature dependence of C only for the lattice component of specific heat (C^{qh}) and is based on the harmonic approximation. Besides, this approximation considers the case of an ideal crystal and does not take into account the presence of defects. Therefore, considering these factors [12], the total specific heat can be represented as:

$$C = C^{qh} + C^{ah} + C^{el} + C^{def}, \qquad (1)$$

where C^{el} is the electronic component of specific heat, C^{ah} is the contribution to the specific heat caused by the anharmonic oscillations of atoms, C^{def} is the contribution to the specific heat of equilibrium point defects [13].

According to [12], the electronic component of the specific heat C^{el} for Bi_2Te_3 can be expressed as $C^{el} = \gamma T$, where $\gamma = 21 \cdot 10^{-5}$ J/(kg·K^2). Hence at room temperature $C^{el} = 0.064$ J/(kg·K^2) which is about 0.04 % of the total specific heat of Bi_2Te_3. Thus, C^{el} at room temperature and above has a very small contribution to the total specific heat.

When analyzing the anharmonic component of the specific heat C^{ah} the harmonic approximation used in Debye's theory is discarded. The dependence of the atom's potential shear energy on its coordinate x is represented as an infinite series:

$$U(x) = \frac{1}{2}ax^2 + bx^3 + cx^4 + \dots \quad . \qquad (2)$$

In the harmonic approximation, only the first term of this series is considered. Taking into account the other terms with the third and higher powers corresponds to the case of the anharmonic approximation. It is known [14] that C^{ah} increases with increasing temperature and can play a significant role when reaching high temperatures.
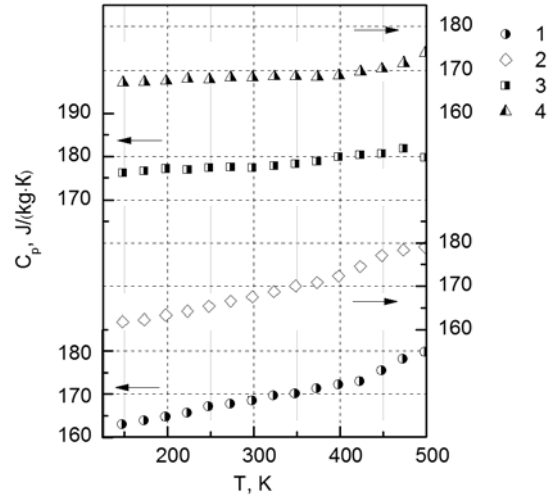

Fig. 2. Temperature dependences of specific heat C_p for $Bi_2(Te_{1-x}Se_x)_3$ solid solutions (*1* — $x = 0$; *2* — $x = 0.0075$; *3* — $x = 0.02$; *4* — $x = 0.06$).

In turn, the maximum contribution to C_p caused by point defects can be observed at pre-melting temperatures [13], when a decrease of the shear modulus of the material leads to the possibility of generating additional defects. The melting temperatures of the solid solution components (T_m (Bi_2Te_3) = 853 K; T_m (Bi_2Se_3) = 983 K [12]) are significantly higher than the range of temperatures at which the measurements were performed ($T = 175$–500 K). Therefore, the temperature generation of new defects in the considered range is unlikely.

Thus, we can assume that the growth of C_p can be naturally associated with the influence of the anharmonic contribution.

Basing on the temperature dependences of C_p, the isotherms of specific heat are constructed (Fig. 3). As was mentioned above, in the study of $Bi_2(Te_{1-x}Se_x)_3$ with a large step in composition [7, 9] the $C_p(x)$ dependence obeyed the additivity law. The increase of x in $Bi_2(Te_{1-x}Se_x)_3$ by $\Delta x = 0.1$ led to a linear growth in C_p by ~ 5 %. A dotted line in Fig. 3 corresponds to the additivity law for the $C_p(x)$ dependences for each temperature. At the beginning of solid solution formation, the addition of the first portions of Bi_2Se_3 to bismuth telluride leads to a slight decrease in C_p. After reaching the composition x ~ 0.005, the trend changes: C_p starts to rise with increasing x and goes through the maximum at x ~ 0.02. After x ~ 0.03 C_p increases gradually up to $x = 0.06$. Thus, for all isotherms, there is a
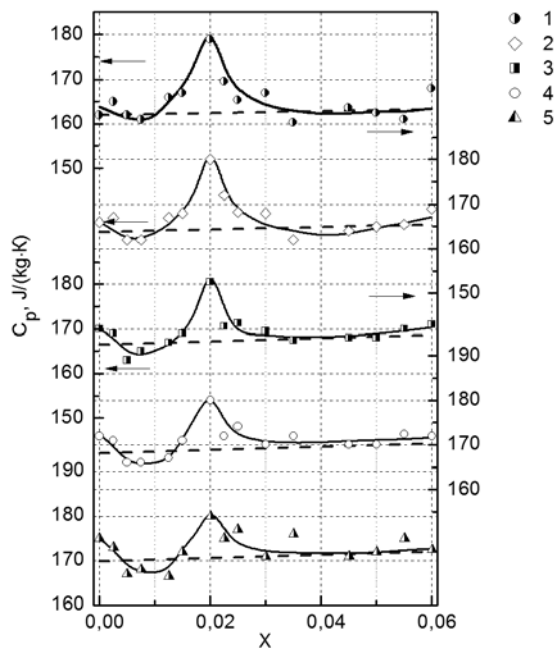
Fig. 3. Dependences of specific heat C_p on the composition x of $Bi_2(Te_{1-x}Se_x)_3$ solid solution at different temperatures (*1* — 175 K; *2* — 225 K; *3* — 300 K; *4* — 350 K; *5* — 400 K, the dotted line marks the change of C_p according to the additivity law).

critical composition $x = 0.02$, at which a maximum is observed on $C_p(x)$ dependences.

It can be assumed that the deviation of the $C_p(x)$ dependence from the additivity law at the beginning of the solid solution formation ($x < 0.01$) may be caused by the difference in the thermodynamics of solid solution formation between diluted and concentrated solid solution. Additive change of C_p is a characteristic feature of substitutional solid solutions. Fig. 3 shows that in the case of a concentrated solid solution ($x > 0.03$) there is indeed a gradual increase in C_p according to the additivity law.

But in the case of the dilute solid solution ($x < 0.01$), when individual Se atoms are introduced into the Bi_2Te_3 matrix and do not interact with each other, the probability increases of their localization not only on positions of Te but also, on anti-structure, interstitial positions, etc. The reach of the free energy minimum in the system is becoming possible with increasing of the configurational entropy of the system and the value of the corresponding entropy term (TS). In this case, the condition of substitution solid solution is not fulfilled and the deviation of the dependence of $C_p(x)$ on the rule of additivity is observed.

The presence of a peak on the C_p isotherms confirms the assumption made in [3, 4] about the realization of the phase transition in the $Bi_2(Te_{1-x}Se_x)_3$ system at $x = 0.02$. To draw a conclusion about the type of this phase transition, it is necessary to analyze the behavior of C_p near the critical point. Let us assume that at $x = 0.02$ the second-order PT occurs. According to the fluctuation theory of second-order PT [15], the properties of the system near the critical point are determined by fluctuations, the correlation radius of which increases sharply when approaching the point of PT and becomes infinite when it is reached. In the vicinity of the critical point, the properties of the system (specific heat, susceptibility, order parameter) change according to power laws. These exponents are called critical indices. The critical index of specific heat (α) for temperature-induced second-order PT was calculated by computer simulation methods and also determined experimentally. When using the Monte Carlo simulation on the three-dimensional (3D) Ising model, the value $\alpha = -0.113$ was obtained in [15]. In various works in the experimental determination of the value of α, there was a large scatter of the obtained values (for example, the values of α for the Curie point of Cr_2O_3 vary from -0.14 to 0.12 [15]).

On the other hand, the anomalous change of properties in the interval $x = 0.0075 \div 0.03$ can be interpreted as a critical phenomenon accompanying the percolation-type transition from dilute to concentrated solid solutions, same as in [3, 4]. Percolation theory explores the phenomena called critical phenomena. They are caused by the properties of the whole ensemble of particles and characterized by the existence of a critical point x_c ("percolation threshold"), where the properties change dramatically. According to the problem of the spheres of percolation theory, when x_c is reached, a chain (infinite cluster) is formed in the crystal, that consists of interacting spheres. In this particular case, deformation fields created around Se atoms when being introduced into the Bi_2Te_3 lattice act as such spheres. Atoms belonging to such a cluster make a joint contribution to the processes of carrier scattering, heat transfer, etc.

Today the analogy [16] is known between the theory of percolation and the fluctuation theory of second-order PT, which are also known to be accompanied by critical phenomena. The theory of critical phenomena was developed for temperature-induced
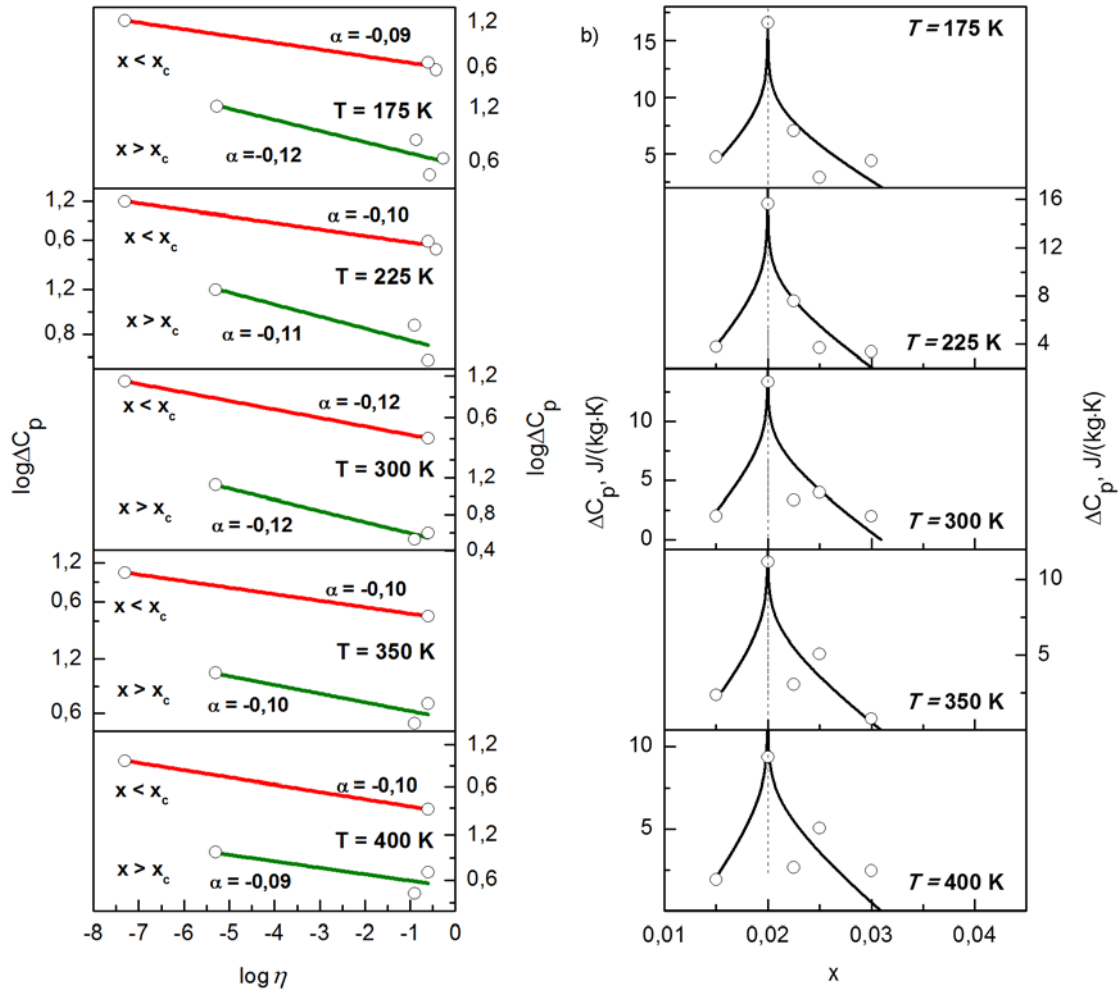
Fig. 4. Dependences of specific heat on solid solution composition at different temperatures a) approximation of the dependence of excess specific heat ΔC_p versus the reduced concentration $(x - x_c)/x_c$ using a double logarithmic scale; b) the dependences of $\Delta C_p(x)$ on the composition near x_c (temperatures are shown in the figure).

second-order PT, but concentration PTs are also well known (Mott, Anderson transition, transitions that occur during the introduction of a ferromagnetic impurity into the paramagnetic matrix, and others). In the case of the concentration-induced transition, the change in properties in the vicinity of x_c can be described both in terms of the percolation theory and of the fluctuation theory of second-order PT by power laws, the critical indices of which are universal and do not depend on the type of system.

To analyze the dependences of specific heat on solid solution composition, we apply the approach used in [14, 17] in the analysis of the critical behavior of C_p in the Bi–Sb system. To determine the critical indices in the $C_p(x)$ dependence, we use the conclusions of the fluctuation theory of second-order PT. By analogy with temperature PT,

the concentration dependence of specific heat near the point of PT can be described as [11, 16]:

$$\Delta C \sim \begin{cases} \eta^{-\alpha} , \\ \eta^{-\alpha'} \end{cases}$$ (3)

where ΔC is the excess specific heat in relation to the additivity law, η is the reduced concentration $(x - x_c)/x_c$, and the critical indices α' and α correspond to the cases of approaching the peak from the sides of lesser and greater concentration values, respectively.

To determine the values of α and α' in (3), we analyzed the $C_p(x)$ dependences near the anomalous peak before $(x < x_c)$ and after $(x > x_c)$ the critical composition. In Fig. 4a a linear approximation of the dependence of the excess specific heat ΔC_p on the reduced concentration η in a double logarithmic scale is presented. Table 1

Table 1. Values of critical indices in vicinity of $x = 0.02$ at different temperatures

T, K	α'/α before x_c/after x_c	interval before x_c/after x_c
175	−0.09/−0.12	(0.0125−0.02)/(0.02−0.03)
225	−0.10/−0.11	(0.0125−0.02)/(0.02−0.025)
300	−0.12/−0.12	(0.015−0.02)/(0.02−0.025)
350	−0.10/−0.10	(0.015−0.02)/(0.02−0.025)
400	−0.10/−0.09	(0.015−0.02)/(0.02−0.225)

shows the values of α' and α for different temperatures. The average value of α for all temperatures is $\alpha = 0.105$, which is close to $\alpha = 0.11$, typical for second-order PT [15] (such as the ferromagnetic-paramagnetic transition, etc. Besides, α does not change significantly when moving from low to high temperatures.

A more accurate approach is used in [15, 17-19] to analyze the shape and position of the peaks in second-order PT. It is based on the assumption of the theory of dynamic scaling that the values of critical indices are assumed to be the same before and after T_c (or x_c): $\alpha' = \alpha = \alpha^{\pm}$. Considering the above, when describing the critical behavior of the temperature dependence of specific heat in [15] and to describe the concentration dependences of C_p in [17, 18] the following expression was used:

$$\Delta C_p = A^{\pm}|\eta|^{-\alpha^{\pm}}(1 - D^{\pm}|\eta|^{\Delta}), \qquad (4)$$

where $\alpha^{\pm}$ is the specific heat critical index, $A^{\pm}$ is the critical amplitude, $D^{\pm}$ is the correction coefficient to scaling, $\Delta = 0.55$. The values of $A^{\pm}$ and $D^{\pm}$ parameters obtained by the least squares method are given in Table 2. In the calculation, the value $\alpha = 0.105$ was used, obtained earlier from (3).

Fig. 4b shows the approximation curves based on (4) with the coefficients from Table 2. The value of x_c obtained from (4) by the least squares method was $x_c = 0.02$ and coincided with the experimentally determined value.

Thus, the results of the study show that the concentration anomalies of electrophysical and mechanical properties, which we observed earlier in the $Bi_2(Te_{1-x}Se_x)_3$ system near $x = 0.02$ [3, 4], are accompanied by a maximum on the concentration dependences of specific heat. The calculated values of the critical index α for the concentration dependences of C_p correspond well to the value of α for temperature-induces second-

Table 2. Values of A^{+-} and D^{+-} coefficients in the vicinity of x_c

T, K	D^+/D^-	A^+/A^-	D^+
175	0.105	0.8	−12
225		0.8	−13
300		0.7	−16
350		0.6	−16

order PT. This confirms the assumption that the percolation PT from dilute to the concentrated solid solution, observed at low impurity content in the $Bi_2(Te_{1-x}Se_x)_3$ system, is a concentration second-order PT.

4. Conclusions

The dependences of the specific heat C_p on temperature ($T = 175–500$ K) and composition ($x = 0–0.06$) are obtained for $Bi_2(Te_{1-x}Se_x)_3$ solid solutions.

It is shown that for all samples in the temperature range under study the specific heat increases with increasing temperature, which is associated with a significant contribution of the anharmonic component to the total specific heat above the Debye temperature.

It is established that at $x \sim 0.02$ an anomalous peak is observed on specific heat isotherms for all temperatures, the presence of which indicates the existence of a phase transition.

The value of the critical index for specific heat ($\alpha = 0.105$) is calculated. It corresponds well to the value of α for specific heat for the second-order temperature-induced phase transitions. The observed composition-induced phase transition is interpreted in terms of the percolation theory as the transition from dilute to concentrated solid solutions.

The results of this work confirm the assumption previously stated [3, 4] that the concentration anomalies observed in the dependences of electrophysical and mechanical properties on the composition of $Bi_2(Te_{1-}$

$_x Se_x)_3$ solid solution are a manifestation of critical phenomena accompanying the concentration second-order phase transition.

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