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MICROCRYSTALLINE, NANOCRYSTALLINE, POROUS,  
AND COMPOSITE SEMICONDUCTORS

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## Determination of Thermodynamic Parameters in the $\text{Cu}_{1.95}\text{Ni}_{0.05}\text{S}$ Phase-Transition Regions

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**Abstract**—X-ray diffraction and differential thermal analysis data obtained in the  $\text{Cu}_{1.95}\text{Ni}_{0.05}\text{S}$  phase-transition region are analyzed. It is established that the low-temperature rhombic  $\alpha$  phase in  $\text{Cu}_{1.95}\text{Ni}_{0.05}\text{S}$  transforms to the hexagonal  $\beta$  phase at temperatures of 370–390 K and to the cubic  $\gamma$  phase at temperatures of 740–765 K according to the scheme  $\alpha \rightarrow \alpha + \beta \xrightarrow{370-390\text{K}} \alpha + \gamma \xrightarrow{740-765\text{K}} \gamma$ . It is determined (using the temperature dependence of differential thermal analysis) that the transition  $\alpha \rightarrow \beta$  is accompanied by heat absorption while the transition  $\beta \rightarrow \gamma$  is accompanied by heat release. It is found that both transitions are allowed and belong to the reconstructive type. Both transitions are found to occur in a fluctuation volume of  $\sim 10^{-20} \text{ cm}^3$  at temperature rates of 0.11 and 0.08  $\text{K}^{-1}$ . It is demonstrated that the transition  $\alpha \rightarrow \gamma$  is accompanied by alternation of the structures passing through the intermediate  $\beta$  phase, which is incommensurate with respect to the  $\alpha$  and  $\gamma$  phases.

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### 1. INTRODUCTION

One of the important aspects of studying phase transitions (PTs) is establishing the correlation between the structural and thermal properties of a material. To determine this correlation, it is necessary to investigate the physical properties of a material in the PT temperature range, which yield information on the PT process. Another topical problem is determination of the distribution of coexisting phases in the PT region. It is well-known that PTs caused by fluctuations in the physical state of a substance lead to variations in the physical properties in this region. The phenomenological theory of smeared PTs [1] is based on the theory of heterophase fluctuations, in which the phase-inclusion function  $L$  characterizing the distribution of coexisting phases in the PT region and its temperature derivative  $dL/dT$  (PT temperature rate) are introduced. As a matter of fact, the function  $L$  can determine the change in all the thermodynamic parameters of a system in the PT region.

Different alloys characterized by a high thermal efficiency [2, 3] have been prepared by substituting atoms of different metals for copper atoms in  $\text{Cu}_2X$  ( $X = \text{S}, \text{Se}, \text{or Te}$ ) chalcogenides. It is worth noting, first, that  $\text{Cu}_2\text{S}$  has the following three polymorphic

modifications [4, 5]: (i) the orthorhombic  $\alpha$  modification stable up to 376.5 K with unit-cell parameters of  $a = 14.90 \text{ \AA}$ ,  $b = 27.28 \text{ \AA}$ , and  $c = 13.41 \text{ \AA}$  (sp. gr.  $\text{Abm}2$ ), (ii) the hexagonal  $\beta$  modification stable at 376.5–708 K with unit-cell parameters of  $a = 3.89 \text{ \AA}$  and  $c = 6.68 \text{ \AA}$ , and (iii) the cubic modification with a lattice period of  $a = 14.90 \text{ \AA}$  (sp. gr.  $\text{Fm}\bar{3}m$ ), which exists at temperatures above 780 K. According to [6], the orthorhombic modification has a unit cell with parameters of  $a = 11.80 \text{ \AA}$ ,  $b = 27.20 \text{ \AA}$ , and  $c = 22.70 \text{ \AA}$ . As was shown in [7], at room temperature  $\text{Cu}_2\text{S}$  has a monoclinic lattice with parameters of  $a = 15.246 \text{ \AA}$ ,  $b = 11.884 \text{ \AA}$ , and  $c = 13.494 \text{ \AA}$  and  $\beta = 116^\circ 35'$  (sp. gr.  $\text{P}2_1/c$ ). In view of the aforesaid, it is of interest to synthesize a  $\text{Cu}_{2-x}\text{M}_x\text{S}$  ( $M = \text{Ni}$  and  $x = 0.05$ ) alloy and study its structure in a wide temperature range.

One of the characteristic materials which undergo PTs is the alloy  $\text{Cu}_{1.95}\text{Ni}_{0.05}\text{S}$ . The X-ray diffraction and thermodynamic parameters of the material at PTs are analyzed. Examination of the different structural characteristics and interacting modifications before the PTs and during them is aimed at establishing the mechanism of their transformations.

**Table 1.** Calculation of the diffraction patterns of the  $\alpha$ -modification of  $\text{Cu}_{1.95}\text{Ni}_{0.05}\text{S}$  at  $T = 300$  K

$d, \text{\AA}$	$I$	$hkl$	$d, \text{\AA}$	$I$	$hkl$	$d, \text{\AA}$	$I$	$hkl$
4.243	6	222	2.659	25	224	1.949	30	116
3.73	20	242	2.609	16	353	1.908	14	662
$d, \text{\AA}$	$I$	$hkl$	$d, \text{\AA}$	$I$	$hkl$	$d, \text{\AA}$	$I$	$hkl$
3.59	16	302	2.555	12	413	1.892	12	216
3.41	6	203	2.524	40	423	1.876	90	2 14 0
3.31	25	180	2.469	45	433	1.797	14	593
3.27	25	420	2.396	85	1 11 1	1.787	14	691
3.18	40	262	2.325	40	174	1.704	35	406
3.15	30	421	2.237	25	205	1.657	12	286
3.051	20	243	2.207	30	225	1.632	10	605
2.942	45	091	2.117	12	444	1.528	25	486
2.873	16	191	2.093	10	194	1.361	10	686
2.755	16	134	2.005	14	345			
2.718	55	044	1.977	100	2 13 1			

**Table 2.** Calculation of the diffraction patterns of the  $\beta$ -modification of  $\text{Cu}_{1.95}\text{Ni}_{0.05}\text{S}$  at  $T = 379$  K

$d, \text{\AA}$	$I$	$hkl$	$d, \text{\AA}$	$I$	$hkl$
3.388	5	002	1.361	2	203
3.055	9	101	1.296	3	210
2.401	88	102	1.281	11	114
1.9805	100	110	1.273	4	211
1.875	98	103	1.143	2	300
1.706	45	200	1.122	3	213
$d, \text{\AA}$	$I$	$hkl$	$d, \text{\AA}$	$I$	$hkl$
1.689	9	004	1.120	3	006
1.661	10	201	1.082	5	302
1.527	6	202	0.975	2	116
1.509	3	104	0.949	2	222

**Table 3.** Calculation of the diffraction patterns of the  $\gamma$ -modification of  $\text{Cu}_{1.95}\text{Ni}_{0.05}\text{S}$  at  $T = 756$  K

$d, \text{\AA}$	$I$	$hkl$
3.345	45	111
2.894	18	200
2.048	10	220
1.746	25	311
1.672	100	222
1.1139	35	333

## 2. FABRICATION OF THE $\text{Cu}_{1.95}\text{Ni}_{0.05}\text{S}$ SAMPLES

The  $\text{Cu}_{1.95}\text{Ni}_{0.05}\text{S}$  alloy was synthesized from initial  $\text{Cu}(99.9998)$ ,  $\text{Ni}(99.90)$ , and high-purity S elements. A quartz cell was filled with the initial substances in amounts required to obtain the desired composition. The cell was evacuated to a pressure of 0.193 Pa. Synthesis was performed in the temperature range of 800–1150°C. To homogenize the composition, the synthesized sample was annealed at a temperature of 800°C for 100 h. Single-crystal  $\text{Cu}_{1.95}\text{Ni}_{0.05}\text{S}$  samples were obtained via slow cooling combined with the Bridgman method.

## 3. EXPERIMENTAL

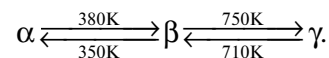
The X-ray diffraction study was carried out using a Bruker D8 ADVANCE diffractometer in the tube mode at 40 kV and 40 mA ( $\text{CuK}\alpha$  radiation,  $\lambda = 1.5406 \text{\AA}$ ) in the temperature range of 300 K <  $T$  < 1400 K using a TTK 450 temperature chamber.

The diffraction reflections were recorded in the angle range of  $0^\circ \leq 2\theta \leq 80^\circ$ . The data obtained upon low-temperature modification of the samples were identified using the TOPAS software package. The crystallographic parameters were refined using the EVA software package. The results obtained are listed in Tables 1–3.

The calculations (see Tables 1–3) show that at room temperature the  $\alpha$  phase has a rhombic lattice with parameters of  $a = 26.50 \text{\AA}$ ,  $b = 15.39 \text{\AA}$ , and  $c = 13.85 \text{\AA}$  (sp. gr.  $Abm2$ ). At a temperature of  $T = (379 \pm 2) \text{ K}$ , it transforms to the hexagonal  $\beta$  phase with parameters of  $a = 3.96 \text{\AA}$  and  $c = 6.78 \text{\AA}$  (sp. gr.  $P63/mmc$ ) and at  $(750 \pm 2) \text{ K}$  passes to the cubic  $\gamma$  phase with a modification period of  $a = 5.788$  (sp. gr.  $Fm\bar{3}m$ ).

Upon sample cooling to a temperature of  $T = 750 \text{ K}$ , the number of diffraction reflections from the  $\gamma$  phase remains invariable. At a temperature of  $T = 730 \text{ K}$ , the sample becomes two-phase: cubic ~60% and hexagonal ~30%. The full  $\gamma \rightarrow \beta$  transformation occurs only at a temperature of  $T = 710 \text{ K}$ . As the temperature is further lowered to  $T = 450 \text{ K}$ , the  $\beta$  phase passes to the hexagonal modification and in the temperature range of 440–460 K there are two phases simultaneously: ~79% hexagonal phase and ~20% rhombic phase. Only at  $T = 350 \text{ K}$  do all diffraction reflections of the rhombic  $\alpha$  modification completely recover.

Thus, it revealed using X-ray diffraction analysis that the PTs in the  $\text{Cu}_{1.95}\text{Ni}_{0.05}\text{S}$  sample in the temperature range of 300–1400 K are enantiotropic and follow the scheme



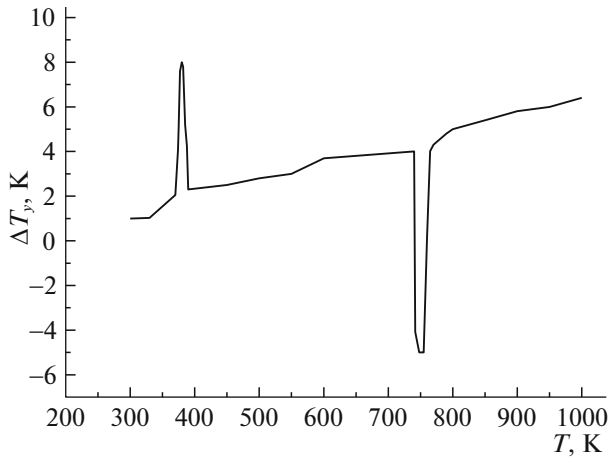


Fig. 1. Temperature dependence of  $\Delta T_y$  in  $\text{Cu}_{1.95}\text{Ni}_{0.05}\text{S}$ .

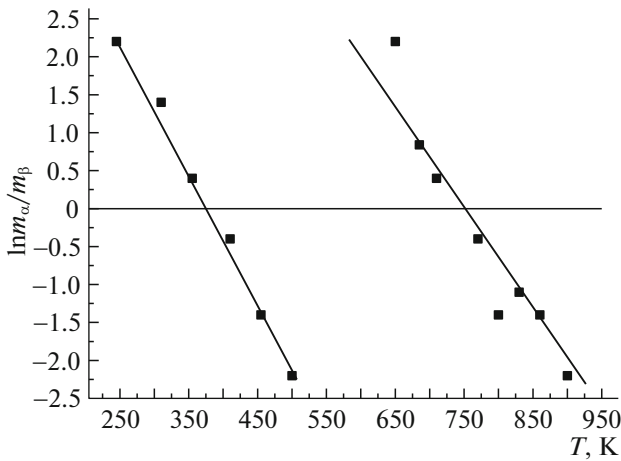


Fig. 2. Temperature dependences of the mass distribution  $\ln m_\alpha/m_\beta$  at the phase transitions in  $\text{Cu}_{1.95}\text{Ni}_{0.05}\text{S}$ .

To establish the correlation between the X-ray diffraction data and thermal processes in the sample under study, we performed similar investigations using differential temperature analysis (DTA) on an STA 600 Perkin Elmer Simultaneous Thermal Analyzer (US). The sample was heated at a rate of 5°C/min. The working gas used was nitrogen and its supply rate was 20 mL/min.

Using the DTA method, we found that in the  $\text{Cu}_{1.95}\text{Ni}_{0.05}\text{S}$  sample heat is absorbed at 370–390 K and released at 740–775 K (Fig. 1).

#### 4. TECHNIQUE FOR DETERMINING THE THERMODYNAMIC PARAMETERS IN THE PHASE-TRANSITION REGION

Within the last fifty years, the theory of smeared PTs has been intensively developed [1, 8–10]. The coexistence of each phase in the PT region was ana-

lyzed. The regularity of the mass distribution as a factor of the temperature was established using the inclusion function  $L(T)$  from the theory of smeared PTs in condensed matter. Denoting the thermodynamic potentials for the  $\alpha$  and  $\beta$  phases as  $\Phi_\alpha$  and  $\Phi_\beta$ , we write for the coexisting phases

$$\Phi(T) = \Phi_\alpha(T) - \Delta\Phi(T)L(T), \quad (1)$$

where  $\Delta\Phi(T) = \Phi_\beta(T) - \Phi_\alpha(T)$ . According to the theory of smeared PTs (SPTs), the inclusion function is [9]

$$L(T) = \{1 + \exp[a_0(T - T_0)]\}^{-1}, \quad (2)$$

where the constant  $a_0$  characterizing the degree of PT smearing depends on the volume of possible phase fluctuations, energy, and temperature of the PT. Taking into account the mass distribution law versus temperature in the PT region, the inclusion function is

$$L(t) = \frac{m_\beta(T)}{m_\alpha(T) + m_\beta(T)} = \left[1 + \frac{m_\alpha(T)}{m_\beta}\right]^{-1}, \quad (3)$$

where  $m_\alpha$  and  $m_\beta$  are the  $\alpha$  and  $\beta$  phase masses, respectively.

Using the temperature dependence  $\ln(m_\alpha/m_\beta(T))$ , we can determine the temperature  $T_0$ , where masses of both phases are quantitatively equal. Using formulas (2) and (3), we obtain

$$a_0 = \frac{1}{T_0 - T} \ln\left(\frac{m_\alpha}{m_\beta}\right). \quad (4)$$

If  $a_0$  is some constant, the factor  $\ln\left(\frac{m_\alpha}{m_\beta}\right)$  should be a linear function of the temperature difference  $(T_0 - T)$  (Fig. 2). Rolov [9] attempted to determine this function via the X-ray diffraction analysis of a solid. He assumed the temperature variation in the X-ray reflection intensities in the narrow coexisting-phase region to be caused by the quantitative phase change. Similarly,  $L(T)$  can also be determined from  $\Delta T_y(T)$ .

For this purpose, it is necessary to ensure the linear temperature variation in  $\ln\left(\frac{m_\alpha}{m_\beta}\right)$  in the transition region. Then, the  $\Delta T$  range for the entire transition can be divided into equal segments and attribute the corresponding values of the investigated effects to the assumed phases, e.g.,

$$\Delta T_y = \Delta T_{y,\alpha} \left(1 - \frac{m_\beta}{m_\alpha}\right) + \Delta T_{y,\beta} \left(\frac{m_\beta}{m_\alpha}\right).$$

**Table 4.** Thermodynamic parameters of  $\text{Cu}_{1.95}\text{Ni}_{0.05}\text{S}$  in the region of the phase transitions

Transition	$T_0$ , K	$a_0$ , $\text{K}^{-1}$	$Q$ , cal/g	$V_{\text{ph}}$ , $\text{cm}^3$	$\Delta H$ , cal/mol	$E_a$ , eV	$B$ , eV	$\Delta S$ , cal/(mol K)	$C_p$ , cal/(mol K)
$\alpha \rightarrow \beta$	380	0.44	34.8	4.6	764	0.18	-0.10	2.01	100.1
$\beta \rightarrow \gamma$	750	0.32	6.0	2.4	958	0.14	-0.06	1.28	92.6

Figure 2 shows the temperature dependences of  $\ln y(T) = \ln \left( \frac{m_\beta}{m_\alpha} \right)$ , where the corresponding masses are determined from the data

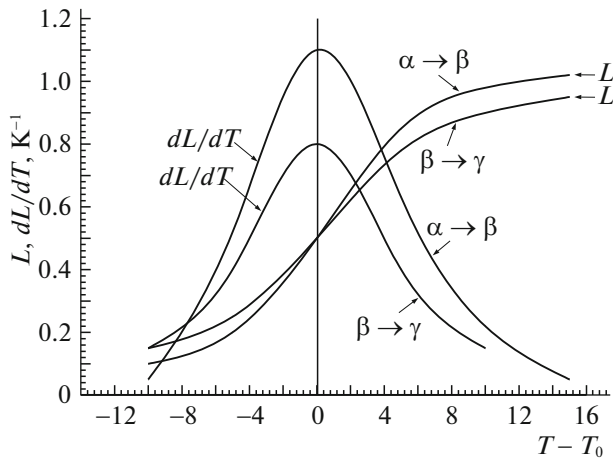
$$\Delta T_y \propto \left( \frac{m_\beta}{m_\alpha} \right) (m_\alpha \sim \Delta T_y; m_\beta \sim \Delta T_{y,\beta}).$$

Using the point of intersection of a straight line with the abscissa axis, we determined the conventional temperatures  $T_0$  of the found PTs, where the two masses are equal. The straight lines in this dependence are described as  $y = \exp[-a_0(T - T_0)]$ , where the  $a_0$  values determined from the slopes of straight lines are the temperature constant of the transition. In all coordinates, the straight lines overlap almost the entire PT region, which is indicative of the validity of the technique used, i.e., determination of the mass distribution law from the temperature dependence as  $m_\beta/m_\alpha(T)$ .

According to the  $a_0$  and  $T_0$  data from formula (2), we determined the inclusion functions  $L(T)$  and their temperature derivatives  $dL/dT$ ,

$$\frac{dL}{dT} = \frac{a_0}{2} \frac{1}{1 + \cosh[a_0(T - T_0)]}, \quad (5)$$

expressing the PT temperature rates. Using the inclusion function, we can determine the behavior and



**Fig. 3.** Temperature dependences of the inclusion function  $L$  and its derivative  $dL/dT$  at the phase transitions in  $\text{Cu}_{1.95}\text{Ni}_{0.05}\text{S}$ .

jumps of different thermodynamic quantities in the PT region.

According to the theory of heterophase fluctuations [8, 9], the constant  $a_0$  is also determined as  $a_0 = V_{\text{ph}0} Q \cdot k^{-1} T_0^{-2}$ , where  $V_{\text{ph}0}$  is the volume of a phase fluctuation and  $Q$  is the amount of heat absorbed (released). Here, the quantity  $V_{\text{ph}0}$  can be considered as the minimum volume in which a sharp PT occurs or the volume of new-phase particles inside the existing phase. The temperature dependence  $V_{\text{ph}}(T)$  can be determined from the formula [11]

$$V_{\text{ph}}(T) = \frac{k T_0^2 a_0}{Q} \frac{1}{2 + \cosh[-a_0(T - T_0)]}. \quad (6)$$

Some important thermodynamic characteristic of PTs, i.e., the transformation entropy and specific heat at arbitrary point  $T_0$ , can be determined using the relations [12]

$$S = -\frac{\partial \Phi}{\partial T} = S_1 + \Delta S L, \quad (7)$$

and

$$C_p = T \frac{\partial S}{\partial T} = C_{p1} + \Delta C_p L + T \Delta S \frac{dL}{dT}, \quad (8)$$

where  $S_1$  and  $C_{p1}$  are the entropy and specific heat before the PT and  $\Delta S$  is transformation entropy. Here,  $\Delta C_p$  is calculated from the data on  $Q$ ,  $\Delta T$ , and  $m$  ( $\Delta C_p = Q/m\Delta T_1$ ), where  $\Delta T_1 = T_{\text{fin}} - (T_{\text{pri}} + vt)$  for heat absorption,  $\Delta T_1 = T_{\text{fin}} - (T_{\text{pri}} - vt)$  for heat release,  $v$  is the heating (or cooling) rate, and  $t$  is the transformation time. The entropy variation in the PT region can be determined as  $\Delta S = \Delta H/T_0$ . The enthalpy variation  $\Delta H$  at the PT is equated with the amount of heat per mole (cal/g) calculated using the DTA (Table 4).

As is known, the temperature dependence of the specific heat in the PT region is determined from the formula [11]

$$C_p = C_{p1} + \frac{a_0 Q}{2m} \frac{1}{1 + \cosh[a_0(T - T_0)]}. \quad (9)$$

An identical calculation was also performed for the transition  $\beta \rightarrow \gamma$ . The data obtained are presented in Figs. 2–4 and in Table 4.

## 5. DATA INTERPRETATION

It is well-known that the structures can pass to one another in different ways. If these phases have low

symmetries, the transition should occur almost without distortions in the crystal symmetry [13], at which the internal energy change should satisfy the condition  $\Delta S/R > \ln 2$  ( $R$  is the universal gas constant) [12]. Such transitions are conventionally referred to as reconstructive PTs.

Tables 1–3 show that the symmetries in  $\text{Cu}_{1.95}\text{Ni}_{0.05}\text{S}$ , which were found in each phase, strongly differ from each other. The  $\text{CuX}$  ( $X = \text{S}, \text{Se}, \text{or Te}$ ) [14] chemical-bond lengths mainly change during the transitions  $\alpha \rightarrow \beta \rightarrow \gamma$  as covalent  $\rightarrow$  covalent ionic  $\rightarrow$  ionic. Consequently, the symmetries and chemical bonds in the  $\text{Cu}_{1.95}\text{Ni}_{0.05}\text{S}$  sample greatly differ for each of the three phases and the transitions satisfy the condition  $\Delta S/R > \ln 2$  (Table 4), since these transitions belong to the reconstructive-type ones. It can be seen from Table 4 that the thermodynamic parameters in the transition  $\alpha \rightarrow \beta$  in  $\text{Cu}_{1.95}\text{Ni}_{0.05}\text{S}$  change much less than those in the transition  $\beta \rightarrow \gamma$ .

This means that the crystal volume or density in the  $\alpha$  and  $\beta$  phases is relatively closer than in the  $\beta$  and  $\gamma$  phases. Therefore, the amount of heat absorbed during the transition  $\alpha \rightarrow \beta$  is smaller than the amount of heat released during the transition  $\beta \rightarrow \gamma$ . This is indicative of the fact that the internal energy between atoms in the structure lattices, which was spent constructing the symmetry at the transitions  $\alpha \rightarrow \beta \rightarrow \gamma$ , increases.

It follows from the above-mentioned factors that the transitions  $\alpha \rightarrow \beta \rightarrow \gamma$  in  $\text{Cu}_{1.95}\text{Ni}_{0.05}\text{S}$  cannot occur without breaking the existing bonds. This circumstance manifests itself also upon a  $dL/dT$  variation, since it is smaller than unity for both transitions. It was shown in [13] that the temperature rate depends on the PT activation energy  $E_a$ , which is determined directly from the DTA data on the investigated sample as  $E_a = RT_{\text{pt}}^2/vt$ , i.e., the energy required for allowance or forbiddance of a transition. The allowance of the transition depends on the  $B$  value, i.e., on the energy-barrier height [13]. The forbidden transition at  $B > E_a$  becomes allowed at  $B < E_a$ . The  $B$  value in  $\text{Cu}_{1.95}\text{Ni}_{0.05}\text{S}$  can be estimated in the following manner. Since both phases satisfy the relations  $N_\alpha \propto \Delta H_\alpha$  and  $N'_\alpha \propto \Delta H_{\alpha \rightarrow \beta}$ , where  $N_\alpha$  is the atomic concentration in the  $\alpha$  phase and  $N'_\alpha$  is the concentration of atoms with energies sufficient to overcome the energy barrier  $B$ , we have  $N'_\alpha = N_\alpha \exp(-B/kT)$ . Under this assumption, we obtain the ratio  $N_\alpha/N'_\alpha \propto \Delta H_\alpha/\Delta H_{\alpha \rightarrow \beta}$ . Then, we can determine the  $B$  value as  $B = kT \ln \frac{\Delta H_{\alpha,\beta}}{\Delta H_\alpha}$ ; the  $\Delta H_\alpha$  value before the PT was taken from [16] ( $\Delta H_\alpha = 17.2$  kcal/mol and  $S_\alpha = 25.5$  cal/(mol K)). Similar calculations were performed also for the transition  $\beta \rightarrow \gamma$ . The obtained  $B$  values are listed in Table 4, where it can be seen that

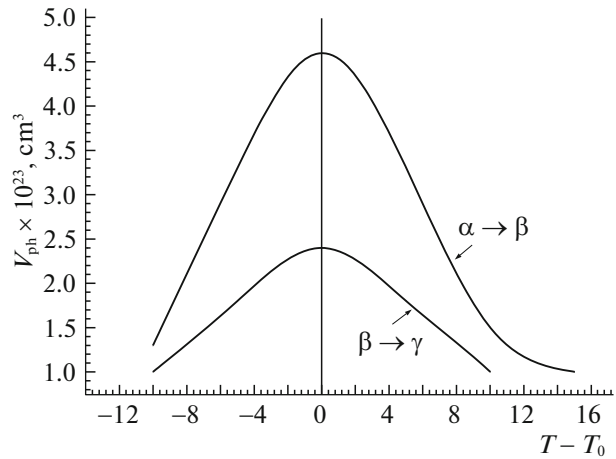


Fig. 4. Temperature dependences of the  $V_{\text{ph}}$  fluctuation at the phase transitions in  $\text{Cu}_{1.95}\text{Ni}_{0.05}\text{S}$ .

$B < E_a$  for both transitions; i.e., both transitions are allowed.

We can assume that the  $B$  energy also leads to the formation of an incommensurate phase. X-ray diffraction analysis revealed the formation of temperature hysteresis during the cycle  $\alpha \leftrightarrow \beta \leftrightarrow \gamma$ . The temperature hysteresis is usually related to the presence of a new incommensurate phase in the existing phase [16, 17]. The role of incommensurability in the transitions is related to the possibility of the pinning of a spatial modulation wave of the incommensurate phase to crystal inhomogeneities, although a certain contribution to the pinning is made by the discrete lattice [17]. This leads to smeared PTs, which are caused by a delay in transformation in the above-described structure and its properties in the incommensurate phase upon a variation in temperature. It can be seen from Tables 1–3 that the ratios between the structural constants in the  $\alpha$  and  $\beta$  phases (as well as in the  $\beta$  and  $\gamma$  phases) are irrational. This gives us grounds to state that the transition  $\alpha \rightarrow \gamma$  is accompanied by the alternation of structures passing through the intermediate  $\beta$  phase, which represents an incommensurate structure with respect to the  $\alpha$ - and  $\gamma$ -phase structures.

One of the key problems in the physics of phase transformations is related to fluctuation of the physical state during the PT. We believe that calculation of the fluctuation volume and distribution in the PT region can be valuable for studying the PTs in  $\text{Cu}_{1.95}\text{Ni}_{0.05}\text{S}$ . We plotted the temperature dependences of  $V_{\text{ph}}$  for the transitions  $\alpha \rightarrow \beta$  and  $\beta \rightarrow \gamma$  (Fig. 4). It can be seen in Fig. 4 that the volume of the fluctuation for both transitions attains its maximum at the point  $T_0$  and asymptotically decreases with increasing distance between  $T$  and  $T_0$ . The fluctuations in the  $\text{Cu}_{1.95}\text{Ni}_{0.05}\text{S}$  crystal were assumed to be caused by temperature inhomogeneities. It can be seen from the  $V_{\text{ph}}(T)$  dependence that the minimum vol-

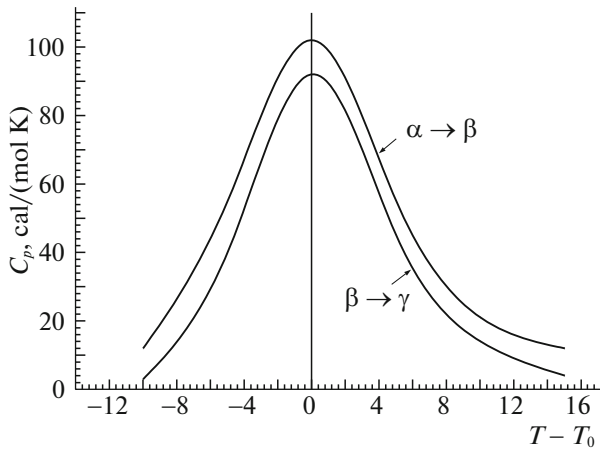


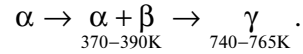
Fig. 5. Temperature dependences of the specific heat  $C_p$  at the phase transitions in  $\text{Cu}_{1.95}\text{Ni}_{0.05}\text{S}$ .

ume of the  $\alpha$ -phase nucleus acting as an inhomogeneity inside the  $\beta$  phase is larger than the volume of the  $\beta$ -phase nucleus inside the  $\gamma$  phase. It is worth noting that the changes in the internal crystal energy with inclusion of the  $\alpha$ -phase nuclei into the  $\beta$  phase and  $\beta$ -phase nuclei into the  $\gamma$  phase lead to temperature inhomogeneity, since the inhomogeneity originates from the polycrystalline structure of the sample. The polycrystallinity is caused by a large difference between the structures of the  $\alpha$ ,  $\beta$ , and  $\gamma$  phases, since the presence of the  $\alpha$  phase in the  $\beta$  phase and  $\beta$  phase in the  $\gamma$  phase leads to  $\text{Cu}_{1.95}\text{Ni}_{0.05}\text{S}$  polycrystallinity.

Another important thermodynamic parameter characterizing the thermal effect is the specific heat of a material. It can be seen in Table 4 that the  $Q$ ,  $\Delta S$ , and  $\Delta H$  values at the point  $T_0$  differ greatly from zero, which indicates that they belong to first-order PTs. At a first-order PT, the temperature dependence of the specific heat should change stepwise. Figure 5 shows that the  $C_p(T)$  dependence is qualitatively similar to the  $\Delta T_y(T)$  dependence (Fig. 1). In the regions of the transitions  $\alpha \rightarrow \beta$  and  $\beta \rightarrow \gamma$ , the  $C_p(T)$  dependence passes through the threshold maximum (Fig. 5). This phenomenon can be explained as follows. It can be seen in Table 4 that, at both PTs, the volume of the phase fluctuation at the point  $T_0$  is estimated as the unit-cell volume, i.e., about  $10^{-20} \text{ cm}^3$ . This gives grounds to suggest that the transition occurs first in one crystal's unit cell. Due to the change in the thermal oscillations of the bond angle, which lead to the formation of local thermal energy, this energy changes with temperature. As the temperature increases, the number of such transformed regions rapidly increases and each local transformation facilitates the transformation of neighboring regions. After attaining the temperature  $T_0$ , all the crystal angles should oscillate with equal amplitudes (the oscillations of the sites become synchronized). Thus, the energy is not transferred from one

side to the other. As a result, at  $T = T_0$ , the  $C_p(T)$  dependence should have a discontinuity; i.e., a singularity of the dependence at the point  $T_0$  should appear. In the experiment, however, the  $C_p(T)$  dependence reaches its final value. This is caused by fluctuations occurring in the following cases: (i) formation of new-phase nuclei in the existing phase, (ii) formation of microstructure of the high-temperature  $\beta$  and  $\gamma$  phases during the transitions  $\alpha \rightarrow \beta$  and  $\beta \rightarrow \gamma$ , and (iii) the formation of crystal inhomogeneities, etc. Each of the listed factors can result in thermal fluctuations leading to the final  $C_p(T)$  value at  $T_0$ . At temperatures of  $T > T_0$ , the inverse process starts, which leads to a decrease in  $C_p(T)$ . A similar analysis was reported in [8], where the magnitude of the thermal fluctuation in the PT regions was shown to be determined by correlation radius.

The data obtained allow us to conclude that the  $\Delta T_y(T)$  extrema closely resemble the similar  $C_p(T)$  dependence. In addition, the  $\Delta T_y(T)$  and  $C_p(T)$  data show that the PT  $\alpha \rightarrow \gamma$  in  $\text{Cu}_{1.95}\text{Ni}_{0.05}\text{S}$  is accompanied by the PTs  $\alpha \rightarrow \beta$  and  $\beta \rightarrow \gamma$ , which follow the scheme



The PT temperatures  $T_0$  determined from the X-ray diffraction data are slightly shifted to the low-temperature region with respect to the data determined from the  $\Delta T_y(T)$  dependence. This can be caused by thermal fluctuations.

Interesting results similar to our data were obtained in [18], where it was established, using the calorimetric study of  $\text{Cu}_{2-x}\text{Se}$ , that the stoichiometric  $\text{Cu}_2\text{Se}$  PT at 414 K experiences a sharp transition  $\alpha \rightarrow \alpha + \beta \rightarrow \beta$ , which is similar to the isothermal (first-order) PT. As the  $x$  value increases, the peaks of the PT  $\alpha \rightarrow \beta$  are spread and the transition temperature decreases to 291 K at  $x = 0.3$ . Starting at  $x = 0.17-0.3$ , the differential scanning calorimeter (DSC) curves contain, along with thermal effects of the eutectoid transformation, the endothermic effect at 189 K, which increases in its absolute value with increasing cooling rate  $v_{\text{cool}}$  up to 5 K/min and shifts toward higher temperatures (257 K), i.e., occurs almost directly before the transition  $\alpha \rightarrow \beta$  and completely vanishes with a decrease in  $v_{\text{cool}}$  to 0.2 K/min. The authors of [18] attributed these transitions to incomplete eutectoid transformation. Summarizing the results obtained, the authors [18] concluded that the transition in the superionic conductivity (SIC) state in  $\text{Cu}_{2-x}\text{Se}$  is a complex eutectic transformation. The occurrence of SIC in the  $\beta$  phase is caused by cationic sublattice disordering in the compound. It was theoretically demonstrated [19] that in the superionic state, where the cation sublattice is completely disordered, the PT transition can be preceded by partial ordering.

It is well-known that all CuX-type ( $X = S, Se,$  or Te) compounds and alloys based on them, e.g.,  $Cu_{1-x}Ni_xX$ , belong to the SIC type [19], in particular, in  $Cu_{1.95}Ni_{0.05}S$ . Interstitial Cu ions have a high mobility and can be ordered below the PT temperature; a slight Cu excess intensifies this process.

## 6. CONCLUSIONS

The complex of experimental studies of  $Cu_{1.95}Ni_{0.05}S$  allows us to conclude that the  $\alpha \rightarrow \gamma$  transition is accompanied by the alternation of structures passing through the intermediate  $\beta$  phase, where the latter is incommensurate with respect to the  $\alpha$  and  $\beta$  phases. We believe that the determined distribution of the ratio between masses of both structures and the minimum fluctuation volume in the PTs and their temperature dependences in the region of each observed PT can yield useful information for studying the PT in  $Cu_{2-x}Ni_xS$  as a whole. Upon removal from the PT in the  $Cu_{1.95}Ni_{0.05}S$  crystal, the sources of fluctuations in the phase states in the region of phase coexistence are temperature inhomogeneities formed by the change in the internal crystal energy and inhomogeneities caused by the large difference between the structures of the  $\alpha$ ,  $\beta$ , and  $\gamma$  phases and the related occurrence of polycrystallinity in the new  $Cu_{1.95}Ni_{0.05}S$  phases in the low-temperature region.

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