SUPERCONDUCTIVITY OF Bi-Sn ALLOYS UNDER HIGH PRESSURE

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A high-pressure X phase is produced in Bi-Sn alloys at a pressure P = 30 kbar and T ≈ 360°K and in a broad concentration range (7.5—90 at % Bi). The critical temperature T_C for alloys in such a structural state exceeds by more than two times the T_C of pure tin, which governs the superconducting properties prior to application of the pressure. With increase of Bi content in the alloy, T_C increases monotonically and $\partial T_C / \partial P$ decreases. Removal of the pressure at 77°K after synthesis causes retention of the metastable state at P = 1 atm. The superconducting parameters of this state are higher than the initial values; thus T_C = 6.5—7.4°K and H_{C2} = 2.8—7.0 kOe for a Bi content ranging from 10 to 80 at.% respectively. The data obtained on the superconducting properties of Bi-Sn alloys agree with the assumptions[15] that the X phase in such alloys is a variable-composition phase based on SnII and BiVII modifications and also that the X phase, SnII and BiVII all possess the same type of crystal lattice. If this is true, then $T_C \rightarrow 7.5°$K for SnII as $P \rightarrow 0$, and $T_C(P)$ should be a nonlinear function. At $P \approx 30$ kbar, $T_C = 8.2 \pm 0.3°$K for BiVII.

$\mathbf{I}$N recent years, interest has increased in investigations of the behavior of superconductors under high pressures. This is attributed to the fact that application of pressure can yield new superconducting modifications of metals and alloys with higher critical parameters. Most published papers pertain to the behavior of pure metals, and only a very limited number of articles deal with the investigation of alloys (see the reveiw[1]).

In this paper we attempt to study systematically the behavior, under pressure, of binary alloys in which both components have high-pressure phases, and also to establish the connection between the phase transformations in these alloys and the superconducting properties. To this end, we chose the system of alloys of bismuth with tin. The phase diagram of this system at atmospheric pressure is of the simple eutectic type[2]. In the entire concentration interval, the alloys have a structure comprising a eutectic mixture of crystals of pure non-superconducting Bi (BiI) and tin (β-Sn or SnI). The critical temperatures and fields T_C and H_{C2} of the alloys are close to the analogous characteristics of the pure polycrystalline β-Sn. Under pressure, both components form a series of superconducting phases, namely SnII ($T_C \approx 5.2°$K at 120 kbar), BiII ($T_C = 3.9°$K at 27 kbar), BiIII ($T_C \approx 7.1°$K at 30 kbar), and BiVI ($T_C \approx 8.3 \pm 0.2°$K at 80 kbar)[1]. The critical parameters of other bismuth modifications, particularly BiVII, have not been determined[1].

Bridgman[5] has observed that at a pressure higher than 20 kbar at 293°K, a new phase is produced in alloys of Bi with Sn having compositions close to equiatomic. Certain T-P sections of the T-P-C phase diagram of the Bi-Sn system have been constructed in[6]. It was established in[7,8] that if the alloys are subjected to a pressure exceeding 20 kbar at a temperature close to 350°K, and are then cooled to 77°K

and fully unloaded, then they retain at atmospheric pressure, up to 170°K, a metastable structure with $T_C \sim 7.8°$K and $H_{C2} \sim 5$—5.5 kOe (at T = 4.2°K). The alloys in the metastable state apparently have a monoclinic crystalline structure. It was also shown that in the concentration interval from 40 to 60 at.% Bi, the structure apparently remains single-phase, and therefore the high-pressure phase (the X phase) is not an intermetallide, as was assumed by Bridgman, but a phase of variable composition of the solid-solution type.

In this connection, an attempt is made in the present paper to answer the following questions: 1) in which concentration interval is the X phase stable under pressure, and how do the T_C of the alloys depend on the composition; 2) is there a connection between the high-pressure modifications of the pure components and the new phase in the alloys; 3) what structural transformations occur during the course of removal of the pressure at different temperatures, and how does this process affect the properties of the alloys?

EXPERIMENTAL PART

We investigated tin alloys having 2, 5, 7.5, 10, 20, 30, 50, 80, 90, 95, and 98 at.% Bi. Samples of given composition were obtained by melting Bi and Sn (>99.999%) under a vacuum of $>10^{-4}$ mm Hg in pyrex ampoules. The melts of the components were thoroughly stirred and rapidly crystallized to prevent liquidation. The ingots were then annealed for more than 100 hours at 373°K in evacuated ampoules. The compositions of the alloys after melting did not differ from the rated values by more than ±0.1 at.%. An investigation of a number of properties of the alloy samples was made both directly under high hydrostatic pressures with the aid of a special low-temperature press[2], and with samples subjected to prior treatment by high pressure

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[1] We use Bundy's [3] designations of the bismuth modifications. In [1] and [4], BiVI is designated BiV.

[2] The construction of the press will be described in greater detail later.

at 293—373°K in a dismountable chamber and "quenched" at 77°K to atmospheric pressure. The loading of the samples to obtain new structural states and to measure T_C as a function of the pressure was performed in a thick-walled cylindrical chamber with inside-channel diameters 2.3—2.6 mm using a procedure close to that in[9]. Rather than the customary beryllium bronze, we used as the material for the high-pressure chamber and for the plungers the new nonmagnetic dispersion-hardening alloy 40KhNYu. This alloy, after optimal heat treatment, has a hardness HRC > 50 and a breaking strength σ_B up to 200 kg/mm². The use of a chamber made of the 40KhNYu alloy and of pistons made of the hard alloy VK-3 or VK-6 makes it possible, without preliminary cold working of the chamber, to produce repeatedly pressures up to 42 kbar, causing practically no plastic deformation of the channel. The chambers under load can also withstand quite well abrupt and repeated temperature changes from 373 to 2°K.[3]

Two cylindrical samples were placed inside the channel of the chamber: one was made of the investigated alloy, and the other of pure tin. The loading and holding of the samples at increased temperature and pressure were effected by placing the press with the chamber in an air thermostat. The temperature in the liquid-helium region was measured with the aid of a gold (+0.07 at.% Fe)-copper thermocouple. The error in the determination of the absolute value of the temperature was not larger than ±0.1°K, and the relative change in the temperature of any one sample at different pressures was measured accurate to ±0.02°K. The error in the measurements of the pressure inside the chamber at room and higher temperatures was ±1kbar, and at T = 2—10°K it amounted to ±2kbar. A control experiment has shown that the pressure drop on the section of the channel where the sample was placed did not exceed ±1.5 kbar. The transition of the samples to the superconducting state was indicated by the usual inductive method.

We measured T_C and H_{C2} at 4.2°K and the thermal expansion in the interval 77—380°K of the samples in the metastable state atmospheric pressure after the action of high pressure. The high pressure at T = 300—350°K was applied to the samples in pyrophyllite ampoules in a simple dismountable chamber of the piston-cylinder type, with external heater. The pressure in the chamber was also calibrated against the transition of the bismuth. All the investigated samples were treated as follows: Loading to 30 kbar at 350°K, holding for 15—20 hours, cooling under pressure to 77°K, unloading and dismantling of the chamber directly in a liquid-nitrogen bath, and extraction of the sample from the ampoule. During the time intervals between the measurements the samples were stored in a dewar with liquid nitrogen.

The measurements of T_C and H_{C2} were performed in installations described earlier[7,10]. A verification has shown that the discrepancies between the absolute values of T_C of the same single-crystal lead sample,

determined both in the chamber of the press and in the apparatus for the measurement of T_C of the samples in the metastable states, do not exceed ±0.1°K. The error in the value of H_{C2} was ±300 Oe. A simple dilatometer was constructed and used to determine the temperatures of the start of the decay of the metastable structures. To register the change in the sample volume during the course of its thermal expansion, a quartz rod with a ferromagnetic pickup on its end was placed on the sample. The pickup moved in a differential transformer having the same construction as that used for the measurement of T_C and H_{C2}, and the same registration circuit was used. The displacement of the rod was calibrated with the aid of an ordinary micrometer head.

RESULTS AND DISCUSSION

We shall analyze the properties of the alloys in the following sequence: we first present data on the behavior of the alloys directly under pressure, and then describe the changes in the properties during the course of the lifting of the pressure and consider the properties of the alloys in the metastable state at atmospheric pressure. In conclusion, we present a possible scheme of the transformations of the Bi-Sn alloys following changes in the pressure and temperature.

1. Superconductivity of Alloys Under Pressure

To determine the concentration interval in which the X-phase is stable, and to establish the values of T_C of the alloys under pressure and the values $\partial T_C/\partial P$, samples of all compositions were subjected to the same treatment directly in the high-pressure chamber. Since prolonged holding is required for the formation of the X phase in alloys with large at.% Bi or Sn, where the diffusion process of mutual dissolution of the components can be protracted, the following schedule was used: loading of the sample together with the standards to ~30 kbar at 295°K, heating to 363°K and soaking for 10 hours, cooling to 293°K, and holding for another 12-15 hours. Then, without removing the load, the press and chamber were cooled together to 77°K and inserted in a helium dewar, and then liquid helium was poured in and the samples were unloaded in steps at ~4—8°K. After each decrease of the load, superconducting transition curves were plotted for the alloy and for the tin, the latter serving as a "manometer."

Figure 1 shows examples of families of the most characteristic transition curves of tin alloys with 50, 90, 95 and 98 at.% bismuth at different pressures. The ordinates represent, in arbitrary units, the changes of the signal on going into the superconducting state.

For the alloys with 2 and 5 at.% Bi, the transitions at P ≈ 30 kbar occurred in the same temperature range (~4.0—4.1°K) as for the quenched solid solutions of Bi in SnI[11]. This shows that no X phase is produced in these alloys at the indicated values of the synthesis pressure and temperature.

The transition curves of all the alloys with 7.5—80 at.% Bi at different pressures have the same shape, and the width of the transition ΔT is sufficiently small (<0.3°K) and is practically independent of the pressure at which the measurements were performed. The
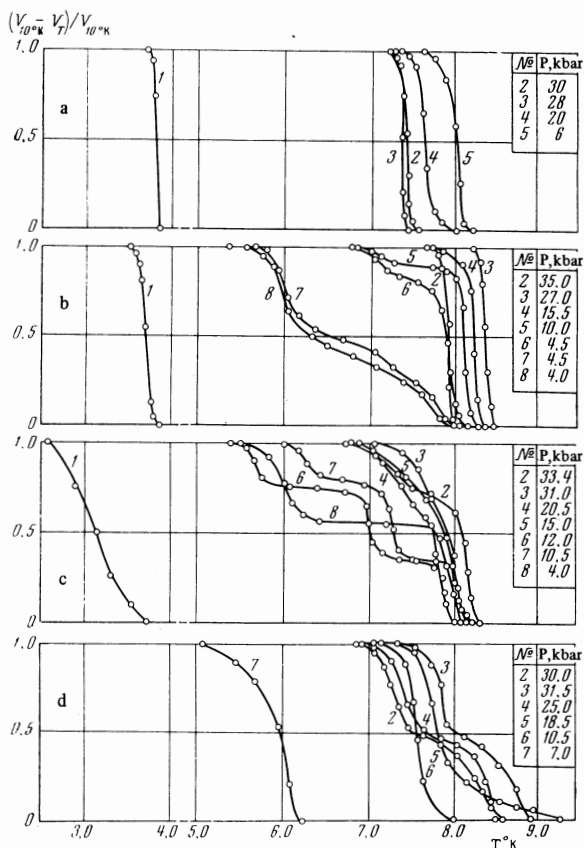

FIG. 1. Superconducting transition curves of alloys of the Bi-Sn system. a—50, b—90, c—95, d—98 at.% Bi. Curves 1 on all the diagrams are the transition curves of the samples in the initial annealed state. Curves 7 and 8 of Fig. b were plotted after heating to 120 and 170°K, respectively, at P = 4.0—4.5 kbar. The ordinates represent the change of the signal on going into the superconducting state.

FIG. 2. Superconducting transition temperatures of alloys of the system Bi-Sn: curve 1—in the initial annealed state (▲), T_c of solid solutions of Bi in β-Sn after quenching (■) [11]; 2—30 kbar; 3—at 20 kbar; 4—at 10 kbar; 5—at P → 0; 6— in the metastable state.

changes in the signal following a complete transition from the superconducting state increase for all these alloys when the pressure is removed. This is undoubtedly due to the elastic expansion of the sample and to the increase of its volume.

Figure 2 shows the values of T_c of all the investigated alloys in the initial state, the annealed state (measurements at P = 1 atm) and at pressures 30, 20, and 10 kbar after synthesis, and also T_c of BiII and BiIII (our data and[1]), BiVI[4], and SnI[12,13]. There are no data on $T_c(P)$ of SnII in the indicated pressure range, since SnII is not stable here, and it is impossible to extrapolate the results of[4], since we do not know the shape of the $T_c(P)$ curve.

Figure 3a shows plots of $T_c(P)$ for alloys with 7.5—90 at.% Bi, while Fig. 3b shows the analogous curves for BiII and BiIII. As seen from these results, all the alloys have close values of the ratio $\partial T_c/\partial P$, which decreases regularly with increasing Bi content. Thus, for the alloys with 7.5 at.% Bi we have $\partial T_c/\partial P = -3.6 \times 10^{-5}$ deg/bar, and for 80 at.% Bi we have $\partial T_c/\partial P = -1.6 \times 10^{-5}$ deg/bar. The values of $\partial T_c/\partial P$ in Bi-Sn alloys with the structure that is produced after the action of the pressure are close in order of magnitude to $\partial T_c/\partial P$ of most nontransition metals[1,14].
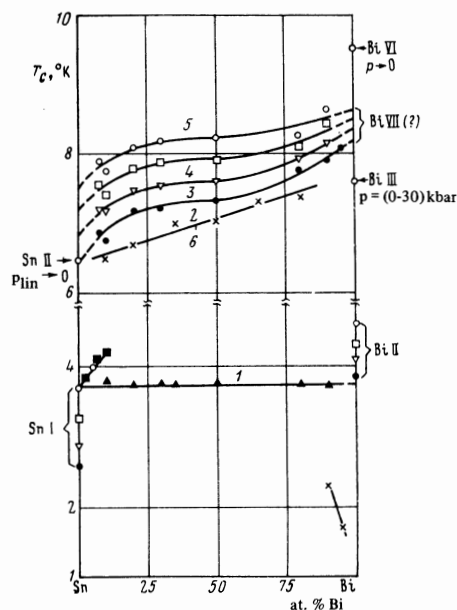
We have already reported earlier[8] that in alloys with 40—60 at.% Bi in the metastable quenched state, according to x-ray analysis data, the structure is practically the same and there is no free Bi or Sn in these alloys. On the other hand, if decay with separation of a phase with another value of T_c (for example, SnI) begins in the alloy[7], or these alloys clearly have a two-phase structure (see below), just as in the cases when Bi ≥ 90 at.%, then this causes immediately a strong "smearing," amounting to several degrees, of the transition curves, or else the appearance on these curves of distinct steps separated from one another by considerable temperature intervals.

Additional proof that there is no bismuth in free form in alloys having a large Bi content and kept at the indicated values of the pressure and temperature is found in the results of the following experiment. A sample with 80 at.% Bi was placed in the chamber and then loaded in the press at 358°K to 28 kbar during one hour. During the time of the loading, the piston displacement was plotted against the press force (curve 1 of Fig. 4). As seen from the plot of the piston displacement against the pressure in the chamber, a kink is observed on the curve, corresponding to the start of the BiI + SnI → X-phase transformation, as well as two distinct jumps due to the BiI → BiII and BiII → BiIII phase transitions. The pressure was then decreased to 19 kbar and kept steady for six hours, and loading to 28 kbar repeated (curve 2). The sample was kept at 28 kbar for a long time, with the pressure periodically decreased and increased in order to register the phase transitions in the bismuth (curves 3, 4, and 5). As seen from the obtained data, the values of the volume effects in Bi transformations decrease with increasing holding time, and as a result of such a
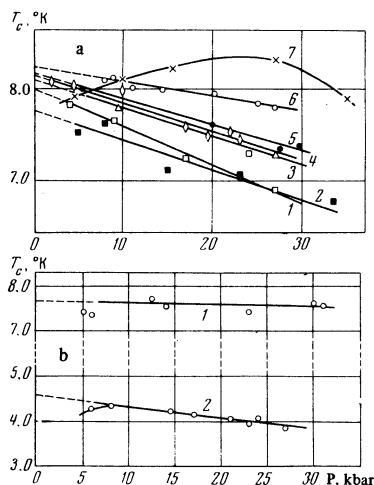
FIG. 3. $T_c(P)$ for the following alloys: a—Sn with 7.5 at.% (1), 10 at.% (2), 20 at.% (3), 30 at.% (4), 50 at.% (5), 80 at.% (6), and 90 at.% (7) Bi; b—BiIII (1) and BiII (2); the decrease of T_c of BiII at ~ 7 kbar was accompanied by a strong decrease of the signal on going into the superconducting state.

treatment almost all of the Bi goes over into the X phase.

Unfortunately, it is impossible to perform such an experiment in our setup on alloys with a large Sn content, owing to the excessively high pressures necessary to register the SnI → SnII transitions. Therefore the data obtained, namely the sharpness of the transitions, the monotonic character of the increase of T_c with increasing atomic percentage of the Bi, the regular variation of $\partial T_c/\partial P$ with changing composition, the absence of excess bismuth in accord with volume-change data, and also the structural data, can be explained by proposing that a new structural state, namely an X phase with high T_c, of the type of variable-composition phase, is produced in Sn alloys with 7.5—90 at.% Bi subjected to a pressure of ~ 30 kbar and a temperature 363—373°K.

Extrapolation of the $T_c = f(\text{at.}\% \text{ Bi})$ curves at P = const (Fig. 2) to pure Sn and Bi leads to interesting results, namely: if pure tin were to go over under
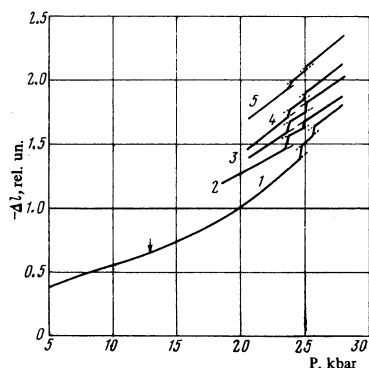

FIG. 4. Loading curves, up to 28 kbar, at v = 0.3 kbar/min, of a sample of Sn alloy with 80 at.% Bi at 358°K (for convenience, the curves are shifted vertically): 1—initial loading (the arrow indicates the pressure at which the Bi + Sn → X-phase transformation begins); 2—after holding for 6 hr at 19 kbar; 3—2 hr at 28 kbar; 4—3.5 hr at 28 kbar; 5—5.5 hr at 28 kbar.

the influence of pressure and temperature into a modification with X-phase structure, then in such a state it would have $T_c \approx 7.5 \pm 0.3°K$ as P → 0, and for Bi in such a case $T_c \approx 8.2 \pm 0.3°K$ as P → 0. Since a sharp discontinuity in the values of T_c of alloys with large Sn content occurs in a narrow concentration interval (5—7.5 at.% Bi), it can be assumed that at P = 30 kbar this is precisely the location of the two-phase region separating the single-phase regions where the alloys with Bi $\lesssim$ 5 at.% have the structure of a Bi-enriched solid solution on the basis of β-Sn with $T_c = 3.7$—4.1°K, while alloys with Bi $\geq$ 7.5 at.% have the structure of the X phase with $T_c > 6.5°K$.

Let us now examine the behavior of alloys with Bi contents 90, 95, and 98 at.%. Whereas for the first of these alloys the transition curves measured after synthesis (curves 2—4 on Fig. 1b) are abrupt ($\Delta T = 0.3°K$), for the other two they are smeared out from 8.3 to 6.8°K and from 8.5 to 7.5°K, respectively (curves 2—4 on Figs. 1c and 1d). The curves show two steps, particularly clearly for the alloy with 98 at.% Bi. However, the alloy with 90 at.% also shows a step near 7.2°K after partial unloading of the sample (curve 5 on Fig. 1b). Such behavior of these three alloys can be understood if it is assumed that in accordance with the phase rule, the single-phase region with X phase on the T-C diagram at P = 30 kbar is separated from the pure bismuth by a two-phase region. (We recall that at 363°K and at 25—40 kbar pure bismuth takes the form of BiIII with $T_c \approx 7.5°K$.) It is therefore natural to assume that under our synthesis conditions the alloy of Sn with 90 at.% Bi lies, at P $\approx$ 30 kbar, on the T-C section of the phase diagram near the boundary with the two-phase region, while the alloys with 95 and 98 at.% Bi lie inside this region, where part of the sample volume is in the form of the X phase, and the excess bismuth is in the form BiIII. (We assume here that no temperature transformations took place in the alloys when they were cooled under pressure.) Then the high-temperature steps on the transition curves should be attributed to the X phase, and the steps near 7.3—7.6°K to BiIII.

In order to establish the slope of the line separating the X-phase region from X-phase + BiIII, we have specially synthesized a sample with 90 at.% Bi not at 90° but at 70°C and P $\approx$ 30 kbar. The transition curve, plotted after such a treatment, was not as abrupt as in the case of synthesis at 90°, and had a step in the region of 7.5°K, just like curve 1 of the alloy with 95 at.% Bi (Fig. 1c), thus evidencing the presence of BiIII. It can thus be assumed with assurance that the region with X phase on the side rich in Bi broadens with increasing temperature and lies above the X phase + BiIII region. This is also corroborated by the fact that extrapolation of the T_c (at.% Bi) plot gives for pure Bi values of T_c in the range 8.1—8.6°K, between the values of T_c for BiIII and BiVI. In addition, the slope of the melting line of the X phase, $\partial T_m/\partial P$, is very close to $\partial T_m/\partial P$ for BiVII[15], and, as is well known, BiVII lies above BiIII on the diagram. Unfortunately, our procedure does not enable us at present to increase P and T to such an extent as to make the alloys with 95 and 98 at.% Bi single-phase, which would make it possible to come all the way to the properties of pure bismuth.

We consider now the question of the possible crystalline structure of the X phase. A thermodynamic calculation of the phase diagram of the alloys of the Bi-Sn system was carried out in[15] on the basis of the experimental data. Inasmuch as the slopes of the lines of melting under pressure of BiVII, the X phase, and SnII are very close, and also on the basis of our old data[8] indicating that the X phase is possibly a solid solution, the authors of[15] have proposed that this phase is a solid solution based on the high-pressure modifications of BiVII and SnII, with a wide region of homogeneity. In addition, they predicted that at $P > 38$ kbar and $T \geq 550°K$, i.e., under conditions when the modifications SnII and BiVII are stable, all the alloys of Bi with Sn should be in a single-phase state, and their structure should be identical to the structures of both BiVII and SnII, and consequently BiVII and SnII should have the identical structure. The results presented here on the superconducting properties of the alloys serve, in our opinion, as experimental proof that such an assumption is correct. A final answer cannot be given at present, owing to the lack of x-ray diffraction data on the structures of BiVII and of the X phase under pressure, and owing to the incompleteness of the data on the structure of SnII. It can be predicted even now, however, that BiVII probably has $T_c \approx 8.2°K$, and for SnII we have $T_c \approx 7.6°K$ as $P \to 0$. If the latter statement proves to be correct, then the $T_c(P)$ of SnII, just as for SnI (see[1]), will be strongly nonlinear. We note that it is practically impossible to determine experimentally the form of $T_c(P)$ of SnII at $P < 50$ kbar using pure Sn, since SnII is stable only at very high pressures.

As is well known, nontransition metals form in rare cases broad single-phase regions. This makes it impossible to draw any generalizing conclusions of the "Matthias rule" type for transition metals, concerning the behavior of T_c of such alloys with changing electron concentration during the alloying process. In[16], a successful attempt was made to obtain a series of solid solutions in films made of Bi and Pb (the compositions ranged from 0 to 100 at.% Pb) with amorphous and crystalline structures, and to measure the dependence of T_c on the concentration. It was shown that in this case, and also in limited composition regions, a monotonic nearly-linear increase of T_c takes place during alloying, when the number of valence electrons per atom increases from 4 to 5, also in a number of other bulky alloy samples. In our case, as seen from Fig. 2, a similar dependence is likewise observed. At the present time it is impossible to compare the results with the theory, as in[16], owing to the lack of the necessary experimental data.

2. Change of Alloy Properties During the Unloading Process

To compare the behavior of alloys and of different modifications of bismuth with decreasing pressure, we measured $T_c(P)$ of polycrystalline samples of pure ($> 99.999\%$) Bi. The samples were subjected to pressures of 26 and 33 kbar at 300°K, corresponding to the stability intervals of BiII and BiIII[3]. Just as in the case of the alloys, the press was cooled with the

chamber under pressure to 4.2°K and the load was removed in steps, with T_c measured after each decrease of pressure. The $T_c(P)$ curves for BiII and BiIII are shown in Fig. 3b. As seen from the plots, upon unloading the BiII begins to change into BiI at 4.2°K near 8 kbar, leading to a lowering of T_c and to a decrease in the magnitude of the signal, and consequently also in the size of the superconducting volume. These decreases are particularly noticeable when the pressure is reduced to 3 kbar. Upon unloading to 3 kbar, the value of T_c of BiIII changed very little, but when the pressure was decreased in the 14−6 kbar interval, noticeable acoustic "clicks" were produced and a jumplike increase in the volume of the sample was revealed by the readings of the strain gauges. At the same time, at each jump, the signal was decreased by a factor of several times on going to the superconducting state, thus evidencing a decrease of the volume in the superconducting phase, i.e., a transformation of some of the BiIII into BiI. Apparently, BiIII, just like BiII, has likewise insufficient metastability, and can go over under certain conditions into the non-superconducting BiI not only when heated to 20°K and at $P = 0$[9], but also at 4.2°K directly under pressure. The remaining superconducting volume of the sample did not change over into BiI at $P \sim 3$ kbar, even after heating to 160°K. The values of $\partial T_c/\partial P$ of both Bi modifications were close to those obtained earlier in[9].

Alloys with 2 and 5 at.% Bi behave during the unloading process in analogy with SnI, and their $\partial T_c/\partial P$ was close to that of pure SnI. As noted above, in alloys with 7.5−80 at.% Bi, unloading at 4.2°K to 2–4 kbar did not lead to the appearance of any singularities on the transition curves. The critical temperatures of the alloys increased with decreasing pressure, and the signals increased monotonically.

The most interesting was the behavior of the alloys of Sn with 90, 95, and 98 at.% Bi (see Figs. 1b–d). Lowering the pressure to 20−24 kbar causes the entire curve of the alloys to shift towards lower temperatures, i.e., $\partial T_c/\partial P > 0$ in this pressure region. The change of T_c differs for different alloys. We wish to note specially that although the experimental error in the determination of the absolute value of the pressure, and the pressure gradient over the chamber, were sufficiently large, we did not encounter in any of the samples of other alloys, in the 30−15 kbar interval, a shift towards lower temperatures of even part of the transition curve when the load on the sample was decreased. In view of the fact that all the experiments were performed under identical conditions, it can be stated that the changes in the sign of $\partial T_c/\partial P$ of the samples with 90−98 at.% are due precisely to the changes of the crystalline or electronic structure of the samples during the unloading process. An additional indication of the possibility of reversal of the sign of $\partial T_c/\partial P$ of Bi compounds is the recently observed analogous effect in Bi_2K, which was studied in detail in[17].

During the course of the reduction in the pressure on the Sn alloy with 90 at.% Bi, a step is produced on the transition curve (curve 5 of Fig. 1b), and the curve becomes similar to curve 2 of the alloy with 95 at.% Bi, measured after the synthesis, whereas in the alloys

with 95 and 98 at.% Bi there occurs a change in the ratio of the magnitudes of the high- and low-temperature steps. This is clearly seen for the alloy with 98 at.% Bi. At $P \lesssim 20$ kbar, $\partial T_c / \partial P$ reverses sign and becomes negative. The removal of the pressure in the region of 13 kbar, in the case of the sample of Sn with 95 at.% Bi, was accompanied by a strong acoustic "click" and, judging from the readings of the strain gauges, by a sharp increase in the volume of the sample. Three distinct steps then appeared on the transition curve at 12 kbar (curve 6 in Fig. 1c), located near 5.8, 7.1, and $8°$K. Further decrease of the pressure in this alloy, to ~ 4.0 kbar (the minimum pressure that could be attained, owing to friction), did not lead to a change in the form of the curve. If the samples were then heated in the chamber, then the transition curve of the alloy with 90 at.% Bi became strongly "smeared" after reaching $120°$K, and became similar to curves 6 and 7 of the alloy with 95 at.% Bi. Further heating, even to $170°$K, did not change the shape of the transition curve. In the alloy with 95 at.% Bi, heating caused the second step to vanish, and left steps of approximately equal magnitude near 5.7 and $8.0°$K, (curve 8 on Fig. 1c). The total signal decreased by an amount equal to the signal from the vanished step. This shows that part of the volume of the sample with $T_c \approx 7.0°$K became non-superconducting after being heated to $90°$K.

In the case of the alloy with 98 at.% Bi (Fig. 1d), a strong change in the shape of the transition curves was observed already during the time of unloading at $4.2°$K (curves 2—5). Indeed, when the pressure was decreased to 10.4 kbar, the high-temperature "tail" on the curve disappeared completely, the curve became much less abrupt, and the superconducting volume, judging from the magnitude of the signal, decreased strongly. With further unloading, one more strong acoustic "click" was observed in the region of ~ 8.5 kbar, after which the superconducting volume decreased, and the entire transition curve (curve 6) shifted to the region of 5—$6°$K. Unloading to 3 kbar and heating to $100°$K caused the superconductivity of the alloy to disappear at $T \geq 2.3°$K.

The following regularity was distinctly observed in the example of these three alloys: the less Sn in the alloy, the smaller the stability of both the X phase and of BiIII. Indeed, in the alloy with 90 at.% Bi, in order to change over part of the X phase to the intermediate state it was necessary to carry out unloading and heating to $120°$K, but even after these operations part of the phase still remained even when heated to $170°$K. In the alloy with 95 at.% Bi, this state occurred during the process of unloading at $4.2°$K, but even here heating to $90°$K did not lead to a complete vanishing of the X phase, although the excess BiIII, as expected, was transformed into BiI. On the other hand, in the alloy with 98 at.% Bi, the X phase experienced martensitic transformations at helium temperatures, and heating to $90°$K led to a vanishing of all the metastable superconducting structural components with $T \geq 2.3°$K.

The formation of one more superconducting phase (which we shall call tentatively the "Y phase") in bismuth-rich alloys unloaded at low temperatures is of considerable interest, all the more since a phase

with $T_c \sim 6.0°$K was recently observed[18] in pure bismuth under unique conditions of "freezing" the pressure. The process whereby the Y phase is produced has a clearly martensitic character, judging from the acoustic "clicks" and the very low temperature at which it takes place. Unfortunately, we have at present no other data hinting at the structure of the Y phase and at its crystallographic connection with the X phase. We can only assume that the Y phase is a certain low-temperature form of Bi doped with small admixtures of Sn, and is intermediate between modifications III and I of bismuth.

3. Properties of Alloys in the Metastable State

To determine the concentrations at which the structures produced after the action of the pressure are metastable, alloys with 5—95 at.% Bi were subjected to a treatment in accordance with the schedule indicated above. We determined T_c and H_{c2} of all the alloys, and the thermal expansion during the course of heating from $77°$K for some of the alloys. The dependence of the mean values of T_c on the composition is shown in Fig. 2 (curve 6). Figure 5 shows the results of the measurements of H_{c2}. As seen from the obtained data, in alloys with 10—80 at.% Bi, after the action of pressure and temperature, the metastable structural state is retained at $P = 1$ atm, with much higher superconducting properties than prior to the high-pressure treatment. Thus, when the Bi content increases from 10 to 80 at.%, the value of T_c of the samples increases linearly from 6.5 to $7.3°$K, and H_{c2} increases accordingly from 2.3 to 7 kOe. In the alloy with 5 at.% Bi, we have $T_c = 4°$K, which is good agreement with the values given by Love[11] for T_c of solid solutions of Bi in Sn obtained by quenching. Consequently, in the alloy with 5 at.% Bi, treatment with temperature and pressure under the conditions indicated above, just as in the case of unloading at $4.2°$K, does not lead to the occurrence of any new metastable structural state, but only transforms pure Bi from the eutectic into a solid solution based on β-Sn.

In alloys with 90 and 95 at.% Bi, the values of T_c are much lower than those of pure tin, and are equal to 2.3 and $1.8°$K, respectively. Two different causes of the lowering of the transition temperature in alloys with large Bi content are possible. In the samples unloaded at $77°$K, the metastable state is not retained and a low-temperature decay of the X phase into Bi and Sn takes place. Since the amount of tin in the alloy is small and it is separated in a matrix of non-supercon-
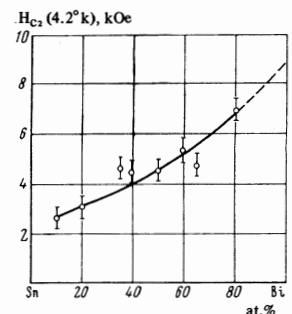

FIG. 5. Dependence of H_{c2} on the composition of the alloys of Bi with Sn in the metastable state after the action of high pressure.
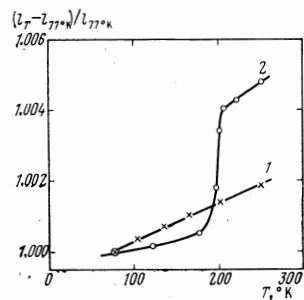
FIG. 6. Curves of thermal expansion of samples of an alloy of Sn with 35 at.% Bi: 1—in the initial annealed state, 2—in the metastable state after the action of high pressure.

ducting BiI, this can cause an appreciable decrease of the T_C of Sn, owing to the "proximity effect" observed in similar cases. Another cause may be the fact that the X phase produced under pressure in the form of a solid solution of Sn in BiVII is unstable and goes over upon unloading into a solid solution based on BiI. Since the separation of the excess tin and the formation of the equilibrium structure by diffusion may be difficult under low-temperature conditions, all that remains is BiI strongly alloyed with tin, which has such transition temperatures. Unfortunately, we were unable to perform an x-ray analysis of the samples after unloading at low temperatures or to determine their structure.
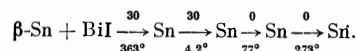
As is well known[2], tin is practically insoluble in bismuth at atmospheric pressure. Therefore, if it turns out that pressure can contribute to the dissolution of tin and to the occurrence of supersaturated metastable solid solutions based on BiI, this would uncover a possibility of investigating the influence of alloying on the superconducting properties of BiI and of tracing their connection with the electronic structure.

An examination of the data on T_C of alloys with 10—80 at.% Bi reveals immediately two singularities in their behavior compared with their behavior under pressure. First, the curves themselves are quite broad ($\Delta T \sim 1.0°K$) and, second, the values of T_C of metastable samples are lower by $1-1.2°K$ than the T_C of samples under pressure as $P \to 0$ (see Fig. 2). All samples with 10—80 at.% Bi in the metastable state, heated in the dilatometer from 77°K, experienced in a narrow temperature interval near 175°K a phase transformation accompanied by an increase in the volume of the alloy. (By way of an example, Fig. 6 shows the expansion curve of the alloy with 35 at.% Bi, the curves for the other alloys being similar.) Their T_C then decreased to 4°K, i.e., it became close to the temperature of β-Sn. The data of[8] show that lines of β-Sn and BiI appear on the x-ray diffraction patterns obtained near 175°K when the metastable samples are heated, i.e., at this temperature the metastable structure breaks up finally into the initial components. However, the volume effects are noticeably smaller in this transformation (by a factor $\sim 2.5-2$) than the effects registered by Bridgman during the production of the X phase[5]. Consequently, during the time of the total unloading in the dismountable chamber at 77°K, an incomplete reverse transformation of the X phase takes place, and proceeds with a positive volume effect that constitutes part of the effect occurring in the
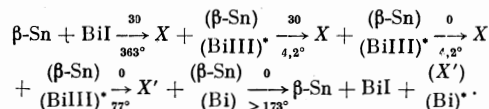
direct Bi + Sn → X-phase transition. This results in a metastable structure that can be designated the X′ phase, and has a critical temperature lower by $\sim 1°K$ and "smeared out" transition curves. It is particularly interesting that H_{C2} of alloys with such a structure are quite high (up to 7 kOe) compared with the H_{C2} of the initial eutectic structure[4]. The effect of strong increase of H_{C2} after the action of the pressure was observed earlier on metastable structures in the alloys Bi-Pb[19] and Tl-Sn[20].

Summarizing the foregoing results, we can propose the following possible sequences of transformations in Bi-Sn alloys upon variation of P and T. (The number above the arrow indicates the pressure in kbar and that below the arrow the temperature in degrees K; the holding time is assumed to be sufficient to attain equilibrium. Solid solutions of Bi in β-Sn or of Sn in Bi will be arbitrarily designated Sn or Bi. The parentheses indicate that the given phase is missing in some alloys; asterisks indicate that only traces of the phase are observed; the Roman numbers are the numbers of the phases.)
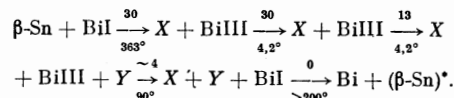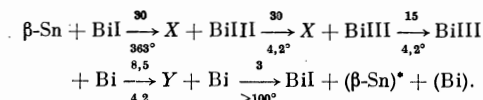
Alloys of Sn with 0—5 at.% Bi:

$$\beta\text{-Sn} + \text{BiI} \xrightarrow[363°]{30} \text{Sn} \xrightarrow[4,2°]{30} \text{Sn} \xrightarrow[77°]{0} \text{Sn} \xrightarrow[273°]{0} \text{SrI}.$$

Alloys of Sn with 7.5—90 at.% Bi:

$$\beta\text{-Sn} + \text{BiI} \xrightarrow[363°]{30} X + \dfrac{(\beta\text{-Sn})}{(\text{BiIII})^*} \xrightarrow[4,2°]{30} X + \dfrac{(\beta\text{-Sn})}{(\text{BiIII})^*} \xrightarrow[4,2°]{0} X$$
$$+ \dfrac{(\beta\text{-Sn})}{(\text{BiIII})^*} \xrightarrow[77°]{0} X' + \dfrac{(\beta\text{-Sn})}{(\text{Bi})} \xrightarrow[>173°]{0} \beta\text{-Sn} + \text{BiI} + \dfrac{(X')}{(\text{Bi})^*}.$$

Alloy of Sn with 95 at.% Bi:

$$\beta\text{-Sn} + \text{BiI} \xrightarrow[363°]{30} X + \text{BiIII} \xrightarrow[4,2°]{30} X + \text{BiIII} \xrightarrow[4,2°]{13} X$$
$$+ \text{BiIII} + Y \xrightarrow[90°]{\sim 4} X + Y + \text{BiI} \xrightarrow[>200°]{0} \text{Bi} + (\beta\text{-Sn})^*.$$

Alloy of Sn with 98 at.% Bi:

$$\beta\text{-Sn} + \text{BiI} \xrightarrow[363°]{30} X + \text{BiIII} \xrightarrow[4,2°]{30} X + \text{BiIII} \xrightarrow[4,2°]{15} \text{BiIII}$$
$$+ \text{Bi} \xrightarrow[4,2]{8,5} Y + \text{Bi} \xrightarrow[>100°]{3} \text{BiI} + (\beta\text{-Sn})^* + (\text{Bi}).$$

There is no doubt that the scheme presented here must be confirmed by direct x-ray structural analysis. A determination of all the details of the structural transformations would be most interesting, since the Bi-Sn system is an excellent model for the study of processes in two-component systems under pressure.

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[4]We shall report later at greater length on the details of the transformations of high-pressure phases in alloys of Bi with Sn upon decrease in pressure and upon heating, and also the possible form of the entire P-T-C phase diagram of the Bi-Sn system.

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66