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Structure of Superconductors. X Thermal, Microscopic and X-ray Investigation of the Bismuth-Palladium System

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A more accurate determination of the phase composition of alloys containing 43–54% by weight Pd is made, and the behavior of these alloys at low temperatures is explained. It is established that increase in the minimum interatomic distances in superconducting compounds of bismuth with palladium leads to an increase in T_c .

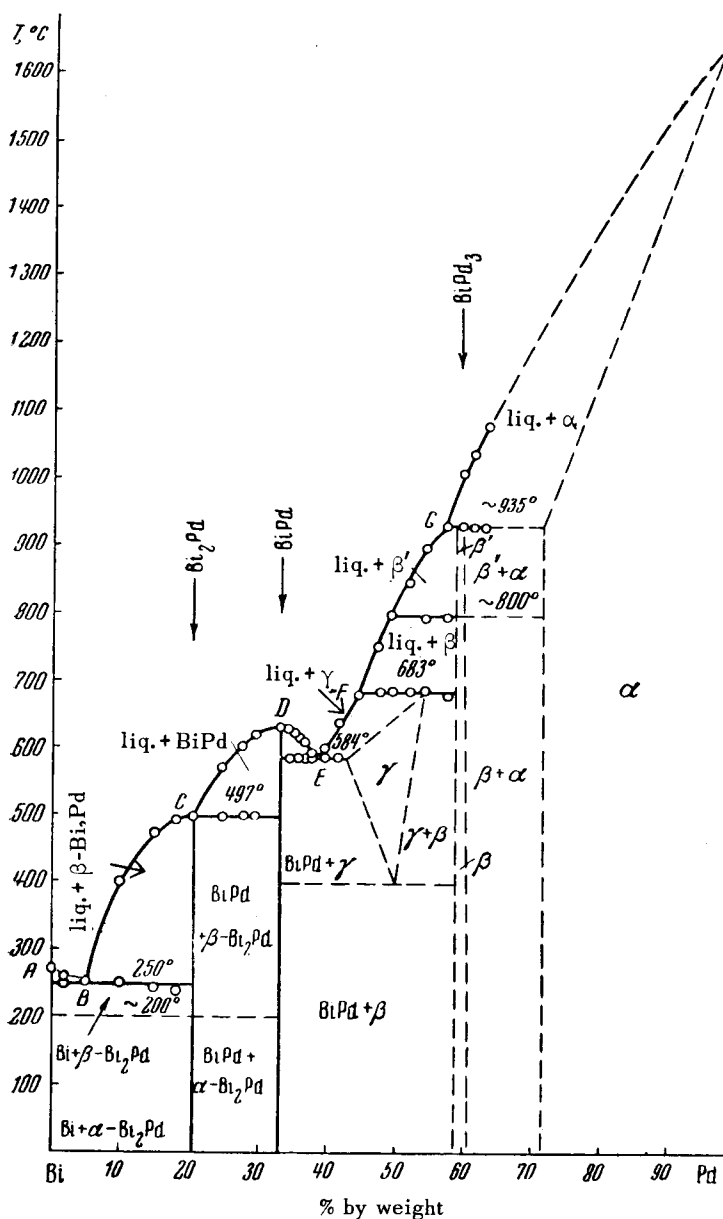
INVESTIGATION OF THE ALLOYS of bismuth with palladium has been undertaken in connection with the study of superconductivity, in view of the fact that certain alloys of this system become superconductors at low temperatures^{1–4}. In this system superconductivity is thus manifested by compounds formed by two non-superconducting elements: bismuth and palladium. From previous microscopic and X-ray investigations of bismuth-palladium alloys, as well as from determinations of the melting temperatures for a series of these alloys, a tentative fusion diagram for the bismuth-palladium system has been constructed.⁵ The crystalline structures of α - and β -Bi₂Pd and of BiPd have been determined,^{6–9} and the low-temperature behavior of variously heat-treated alloys has been explained.^{4,5,10} The present study was undertaken with the object of determining whether there is any connection between the atomic-crystalline structure of these alloys and their superconducting properties and with the further object of determining more precisely the phase composition of certain alloys and explaining their behavior at low temperatures.

THERMAL ANALYSIS

Chemically pure bismuth and palladium were employed in the preparation of the alloys; melting was

accomplished in a resistance oven, in quartz capsules under an argon atmosphere. The heating and cooling curves were recorded with the aid of an automatic electronic potentiometer EPP-09 to temperatures of 200–400°C. The weights of the alloy samples ranged between 0.5 and 2 g. One curve having been recorded, the requisite amount of bismuth or palladium was added to the alloy; the latter was maintained for some time at an elevated temperature, and then the next curve was taken. Curves were recorded in this manner over a certain concentration interval (10–20% by weight), following which the alloy was replaced by a freshly-prepared mixture of bismuth and palladium, to avoid the accumulation of errors in the concentration.

The results obtained in this thermal analysis are represented graphically in Fig. 1. As palladium is added to the bismuth, the liquefaction temperature falls along *AB*. Beginning with ~ 5% by weight Pd, the liquefaction curve rises progressively along *BC*, and at 20.3% by weight Pd reaches a transition point at a temperature of 497°; at this temperature the compound Bi₂Pd liquefies with decomposition. The next branch of the liquefaction curve, *CDE*, beginning at 20.3% by weight Pd, rises as the palladium content of the alloys increases and reaches its peak at 33.8% by weight Pd, corresponding to the compound BiPd. Further addition of palladium



causes the liquefaction curve to fall; eutectic points are found on the cooling curves at $\sim 584^\circ$. The temperatures at which crystallization of the γ -phase becomes complete and the transition to the solid state occurs (eutectoid decomposition) could not be determined, owing to the inadequate sensitivity of the apparatus. The branch EF corresponds to initial precipitation of the γ -phase.

The compound BiPd_3 (β -phase) liquefies with decomposition at a temperature of 935° . The branch FG corresponds to initial precipitation of crystals of BiPd_3 (β -phase). On the cooling curves for al-

loys with concentrations of 55 and 58% by weight a weak thermal effect was observed at $\sim 800^\circ\text{C}$ which is related to a polymorphic transition of the compound BiPd_3 (β -phase). Thermal analysis was not carried out for the palladium-rich alloys, in view of their high melting temperatures.

Information is encountered in the literature regarding an X-ray study of the compound Pd_5Bi_3 , which, according to the data of Ref. 11, crystallizes in two modifications: one high-temperature and the other low-temperature. For the high-temperature modification a structure of the type corre-

sponding to nickel arsenide, with $a = 4.50 \pm 0.05$ kX and $c/a = 1.29$ is specified; for the low-temperature modification a low symmetry is indicated.

The results of our microscopic and X-ray studies in this composition range, however, show that in the temperature interval $400 - 680^\circ\text{C}$, there crystallizes a γ -phase having a rather large region of solubility and resembling the γ -phase of the antimony-palladium system,¹² rather than a compound having a definite stoichiometric composition (Pd_5Bi_3).

MICROSTRUCTURE AND X-RAY PHASE ANALYSIS

Investigation of the microstructure was carried out with alloys specially prepared for this purpose. The following etching agents were used in studying the microstructure: an aqueous mixture of $\text{KI} + \text{I}$, primarily for alloys containing large proportions of bismuth, and nitric acid and aqua regia, for alloys rich in palladium. The palladium-poor (hypoeutectic) alloys consist of bismuth and $\text{Bi}_2\text{Pd} + \text{Bi}$ eutectic. Alloys containing less than 20.33% by weight Pd are composed of crystals of Bi_2Pd and $\text{Bi}_2\text{Pd} + \text{Bi}$ eutectic. The number of precipitated Bi_2Pd crystals increases with increasing palladium concentration. Since Bi_2Pd can crystallize in two modifications,⁷ alloys in this composition range when cooled rapidly from a temperature above 200°C consist of eutectic and Bi_2Pd crystals of the high-temperature modification ($\beta\text{-Bi}_2\text{Pd}$), while annealed alloys are composed of eutectic and Bi_2Pd crystals of the low-temperature modification ($\alpha\text{-Bi}_2\text{Pd}$).

The temperature of the polymorphic transition in Bi_2Pd cannot be determined from the thermal analysis data, since the thermal effect, due to its small magnitude and the inadequate sensitivity of the apparatus, was not observed on the cooling curves. It may be presumed, however, that this temperature lies in the vicinity of 200°C , since alloys annealed at 350°C and then rapidly cooled from that temperature contain $\beta\text{-Bi}_2\text{Pd}$, while a $\beta\text{-Bi}_2\text{Pd}$ alloy annealed for three hours at 195°C shows an intermediate condition, namely, an incomplete transition from the β to the α -modification is observed. The powder X-ray pattern obtained from such an alloy, characterized by a strong background, contains primarily the lines of $\alpha\text{-Bi}_2\text{Pd}$. Metallographically, a unique structure is observed (Fig. 2), differing from the structures of the annealed and quenched alloys.

Alloys in the region between 20.33 and 32.8% by weight Pd are two-phase, and consist of crystals of

Bi_2Pd and BiPd . Rapidly-cooled alloys consist of crystals of $\beta\text{-Bi}_2\text{Pd}$ and BiPd . Annealed alloys consist of crystals of $\alpha\text{-Bi}_2\text{Pd}$ and BiPd . Powder X-ray patterns obtained from annealed and quenched alloys of the proper composition for BiPd (33.78% by weight Pd) are identical, precluding polymorphism in this compound.

Annealed alloys in the region from 32.8 to 33.8% by weight Pd are homogeneous, which suggests a small solubility of bismuth in BiPd . An attempt was made to confirm this metallographically-observed small solubility of bismuth in BiPd by X-ray methods. In the X-ray patterns obtained from polycrystalline samples of these alloys with radiations from copper in a chamber 86 mm in diameter no appreciable displacement of the back-reflected lines was observed. In alloys in the region from 33.8 to 43% by weight formation of a eutectic was observed, the eutectic point corresponding approximately to a concentration of 38% by weight Pd.

Hypoeutectic alloys rapidly cooled from a temperature above 400° consist of crystals of BiPd and $\text{BiPd} + \gamma$ -phase eutectic (Fig. 3). Annealing of these alloys at temperatures below 400° leads to decomposition of the γ -phase. Figure 4 shows a photomicrograph of such an alloy, in which dark etched BiPd crystals can be seen in a matrix of $\text{BiPd} + \beta$ -phase (BiPd_3) eutectoid. Ordinarily annealed hypereutectic alloys containing up to 43% by weight Pd consist of $\text{BiPd} + \gamma$ -phase eutectic and γ -phase. Figure 5 shows a photomicrograph of a hypereutectic alloy, in which within the eutectic matrix there can be seen crystals of the γ -phase, surrounded by layers of the depleted eutectic. The presence of these layers gives some indication of variability in the composition of the γ -phase.

With rapid cooling, the formation of homogeneous alloys is observed in the region 43–54% by weight Pd, which implies the existence of a solid solution in this concentration interval. Varied heat treatment of alloys in this concentration region leads to variation of the alloy structure. Reducing the rate of cooling causes precipitation of the solid solution (γ -phase). Thus, for example, an alloy containing 48% by weight Pd when cooled with the capsule in the open air is found microscopically to have a homogeneous structure. Reducing the rate of cooling for this alloy leads to precipitation of a phase rich in palladium (β -phase) (Fig. 6). The structure of this alloy, with its characteristic alternation of light needles (more probably platelets) with dark zones, is similar to the structures found

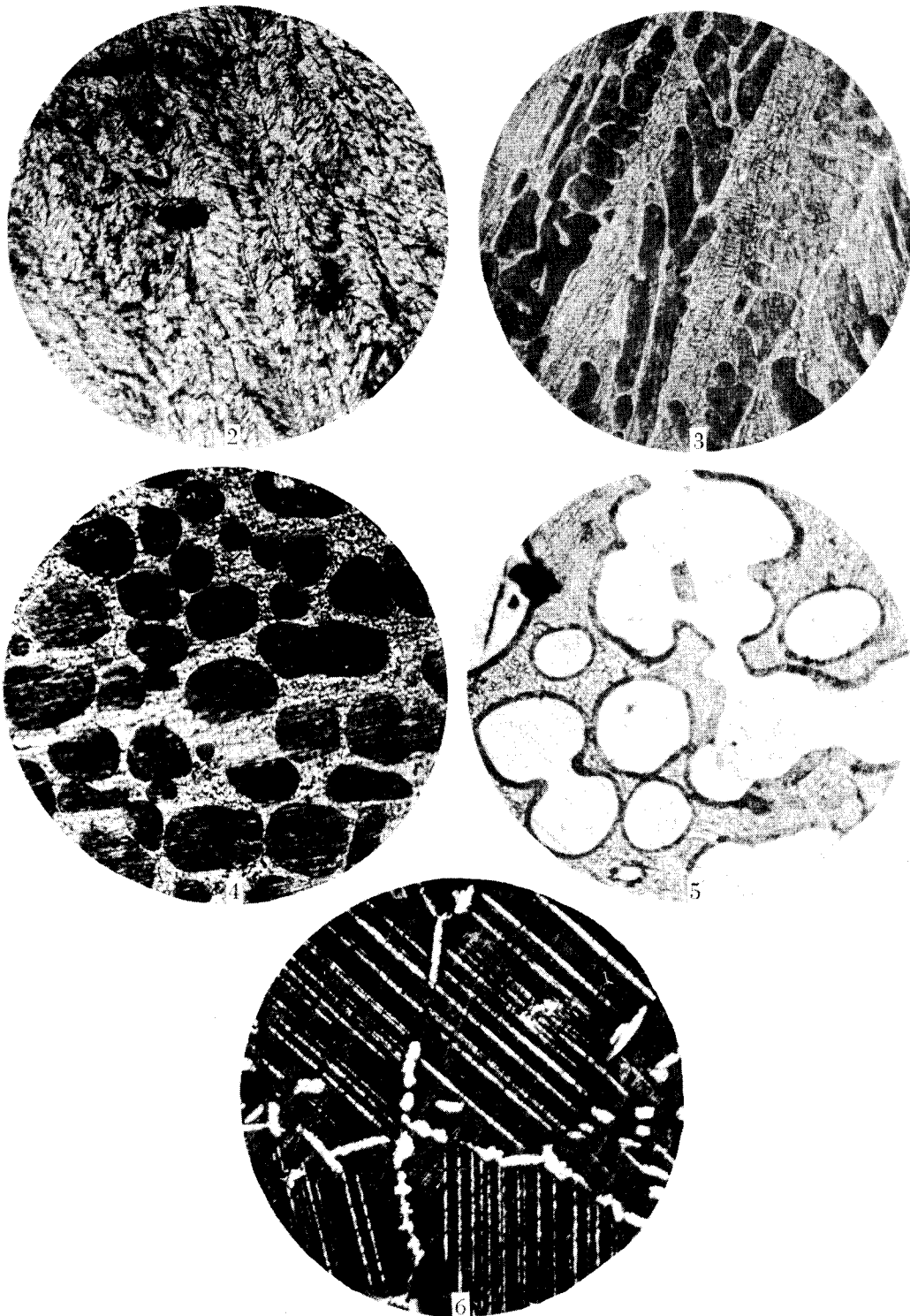


FIG. 2. Etched in KI + I; magnification 383 $\times$.

FIG. 3. Etched in KI + I; magnification 383 $\times$.

FIG. 4. Etched in KI + I; magnification 383 $\times$.

FIG. 5. Etched in KI + I; magnification 201 $\times$.

FIG. 6. Etched in HNO_3 ; magnification 201 $\times$.

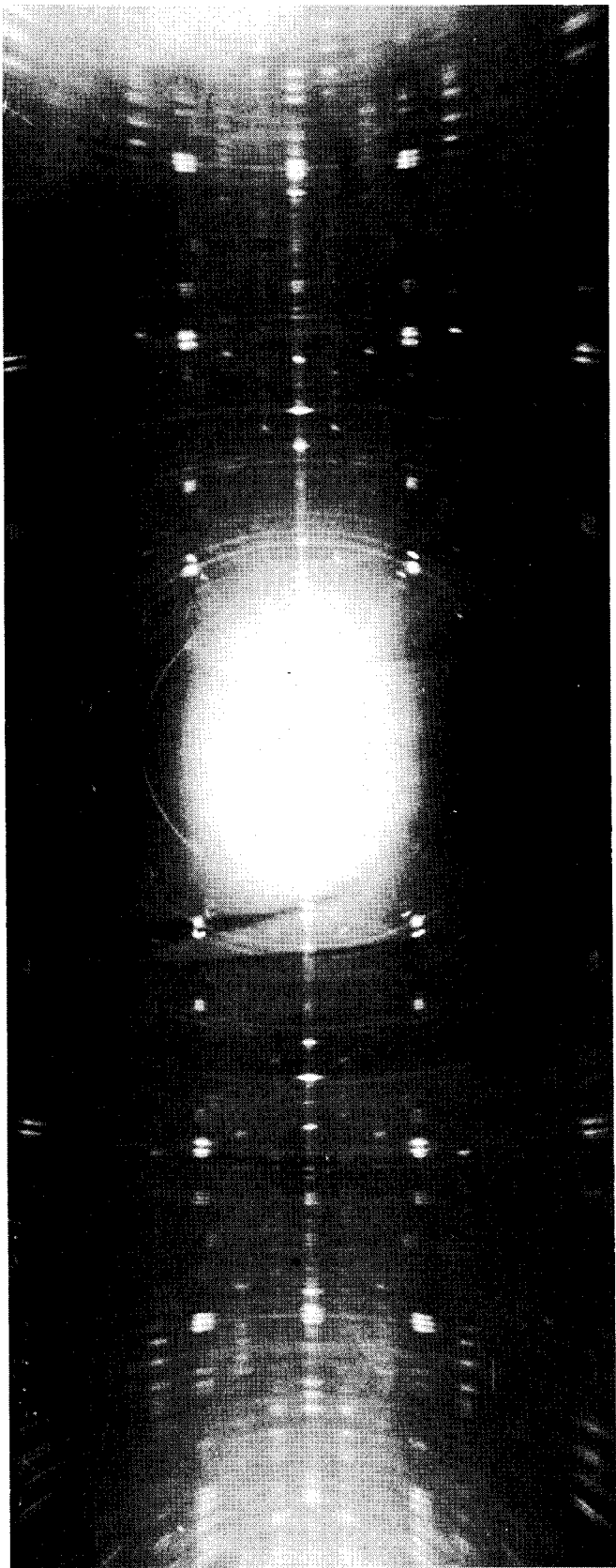


FIG. 7

in the analogous range of alloys in the antimony-palladium system, as reported in the work of Grigor'ev.¹² The light areas represent precipitation in the solid state of the palladium-rich phase (β -phase), while the dark matrix is the γ -phase. After prolonged annealing at a temperature of 250° C this structure changes sharply: the laminar formation is replaced by a typical pattern characteristic of eutectic mixtures containing, in addition, a certain amount of the superabundant component; i.e., a structure similar to that represented in the photomicrograph in Fig. 4 is observed, in which, however, the number of BiPd crystals is smaller, in accordance with the composition. With insufficient annealing the decomposition of the γ -phase remains incomplete.

Powder X-ray patterns obtained for variously heat-treated alloys in this concentration range show against a strong background a small number of diffuse lines, from which it is difficult to determine definitely the phase composition of the alloy. Sharp lines were obtained only in the powder X-ray patterns for the γ -phase.

From a homogeneous alloy of composition 43.5% by weight Pd, cooled to the temperature of liquid air, segments were detached having the form of platelets with two well-formed plane surfaces giving ideal optical reflection. From the Laue and X-ray rotation patterns obtained with these crystalline concretions it was determined that the γ -phase crystallizes in a hexagonal lattice with constants $a = 7.75 \pm 0.05$ kX and $c = 5.85 \pm 0.05$ kX. The unit cell contains about 16 atoms of bismuth and palladium. The γ -phase has a super-lattice of the nickel arsenide type. For an alloy composition of 43.5% by weight Pd the pseudo-cell for the γ -phase has the parameters $a = 4.45$ and $c/a = 1.31$.

These γ -phase crystals were annealed for 8 hours at 250° C. X-ray rotation patterns were obtained from the annealed crystals (Fig. 7). In these X-ray rotation patterns, in addition to interference from the monocrystals, there appeared interference lines which were absent in the X-ray patterns for the un-annealed crystals. From the calculated interplanar distances and the intensities of the lines it was established that these correspond to two crystal lattices — BiPd and the low-temperature modifications of BiPd₃ (β -phase). Thus formation of two compounds as a result of annealing a homogeneous crystal of the γ -phase characterizes the eutectoid decomposition of this solid solution and confirms the metallographic data.

Alloys of composition corresponding to BiPd₃ (60.49% by weight Pd), both rapidly cooled and annealed, are metallographically homogeneous, but the powder X-ray patterns obtained for these alloys differ, from which it may be asserted that polymorphism occurs in this compound. This is confirmed by the differing solubilities of the annealed and quenched alloys in acids. Annealed alloys are more readily dissolved in HNO₃ than quenched alloys. It is probable that the compound BiPd₃ can exist over a certain concentration interval, since alloys containing 57% by weight Pd are nearly single-phase.

Alloys in the concentration interval from 60.49 to ~ 72% by weight palladium consist of crystals of a solid solution of bismuth in palladium and BiPd₃ (β -phase). With rapid cooling of the alloy, the solid solution of bismuth and palladium crystallizes in the form of dendrites, while annealed alloys are observed to contain crystals of irregular form. Alloys more rich in palladium, in the region up to 28% by weight Bi are found to be homogeneous after prolonged annealing, and represent a solid solution of bismuth and palladium. It has been established by X-ray methods that the maximum variation in the linear dimensions of the lattice for the solid mixture is about 3%.⁷

DENSITY, MICRO-HARDNESS AND TRANSITION TEMPERATURES FOR COMPOUNDS IN THE SUPERCONDUCTING STATE

The density σ_{hydr} of the compounds was determined for ingots weighing between 0.5 and 2.5 g by the method of hydrostatic suspension¹³ in carbon tetrachloride ($\sigma_{\text{pycn}} = 1.585$ g/cm³) or bromoform ($\sigma_{\text{pycn}} = 2.885$ g/cm³).

Table 1 gives the densities σ_{hydr} and σ_X , the latter calculated from the X-ray data at room temperature.

The micro-hardness of the compounds was measured in the apparatus PMT-3, with a constant loading of 10 g on the indenter. The measurements were made on several samples from various melts, and the results were averaged. Table 1 also gives the average values of the micro-hardness and their limits of dispersion. For α and β -Bi₂Pd and the β and β' phases (BiPd₃) the scatter in the micro-hardness lies within the limits of error for the measurement, but for BiPd and the γ -phase it exceeds the limits of error, which may be explained by variation in the alloy composition and by anisotropy. For some of the ordinarily-annealed BiPd₃ samples the

TABLE 1

Compound	$\sigma_{\text{hydr}}, \text{g/cm}^3$	$\sigma_X, \text{g/cm}^3$	Average micro-hardness, kg/mm^2	Limits of variation in micro-hardness	$T_c, ^\circ\text{K}$
$\alpha\text{-Bi}_2\text{Pd}$	11.5	11.65	170	140—200	1.7
$\beta\text{-Bi}_2\text{Pd}$	11.7	11.87	135	120—150	4.25
BiPd	12.5	12.56	200	130—270	3.7
γ -phase					
(composition 43.5% by weight Pd)	12.7	—	400	360—430	3.7—4
(composition 50.5% by weight Pd)	12.7	—	360	280—420	
BiPd_3 (β -phase)	12.8	—	230	185—280	—
BiPd_3 (β' -phase)	12.9	—	150	135—210	—

average values of the micro-hardness approached the micro-hardness for the γ -phase.

A study of the superconducting properties of bismuth-palladium alloys has been carried out by Alekseevskii, *et al.*,¹⁻⁴ at the Institute of Physical Problems, Academy of Sciences, U.S.S.R. Table 1 gives the temperatures T_c of the transition to the superconducting state for alloys of bismuth and palladium. The compounds α and $\beta\text{-Bi}_2\text{Pd}$ and BiPd are superconductors. The transition to the superconducting state for the γ -phase at temperatures near T_c for BiPd may be occasioned by partial eutectoid decay in the samples, in which case the superconductivity of the latter would be due to the BiPd crystals, or, alternatively, T_c for the γ -phase

may be near in value to T_c for BiPd. The compound BiPd_3 does not appear to be a superconductor.

DATA FROM THE STRUCTURAL STUDIES

1) The *low-temperature modification* $\alpha\text{-Bi}_2\text{Pd}$ crystallizes in a monoclinic lattice^{6,7} with constants $a = 12.74 \pm 0.01$ Å; $b = 4.25 \pm 0.02$ Å; $c = 5.665 \pm 0.005$ Å; $\beta = 102^\circ 35' \pm 10'$. The unit cell is centered on the (001) face and contains four molecular masses, corresponding to 12 atoms. The space group C_{2h}^3 , or $C 2/m$. The bismuth and palladium atoms are distributed in symmetry planes, in fourfold complexes (4i).

The structure of $\alpha\text{-Bi}_2\text{Pd}$ is of a new type.

Table 2 gives the interatomic distances, the coordinates of the atoms, and the number of neighbors.

TABLE 2

Atom	Complex	x	y	z	Number of neighbors	Interatomic distances, Å
Bi I	4 i_1	0.156	0	0.321	4 Pd	2.78; 2.83; 2.83; 3.15
Bi II	4 i_2	0.076	1/2	0.796	3 Pd	2.90; 2.90; 2.87
Pd	4 i_3	0.226	0	0.820	7 Bi	2.78 2.83; 2.83; 2.90; 2.90; 2.97; 3.15

2) The *high-temperature modification* $\beta\text{-Bi}_2\text{Pd}$ crystallizes in a tetragonal lattice⁷ with constants $a = 3.362 \pm 0.001$ Å; $c = 12.983 \pm 0.001$ Å; the unit cell contains two molecular masses. The space group is D_{4h}^{17} , or $I4/mmm$. The two palladium atoms are located at the position 2(a), the four bismuth atoms at the position 4(e). The parameter for the bismuth atoms is $Z = 0.363$. The structure of $\beta\text{-Bi}_2\text{Pd}$ is of a new type. The α and $\beta\text{-Bi}_2\text{Pd}$ modifications are connected with each other structurally.

The interatomic distances are given in Table 3.

3) The *compound* BiPd crystallizes in an ortho-

rhombic lattice^{7,8} with constants $a = 7.203 \pm 0.001$ Å; $b = 8.707 \pm 0.002$ Å; $c = 10.662 \pm 0.001$ Å. The unit cell is centered on the (001) face and contains

TABLE 3

Atoms	Experiment	ΣR
Bi — Bi	3.362	3.10
Bi — Bi	3.64	3.10
Bi — Pd	2.97	2.92

16 molecular masses, corresponding to 32 atoms. The space group is C_{2v}^{12} , or $Ccm2_1$. The structure of BiPd is of a new type having no center of symmetry.

The interatomic distances, the coordinates of the atoms, and the number of neighbors are listed in Table 4.

TABLE 4

Atom	Complex	<i>x</i>	<i>y</i>	<i>z</i>	Number of neighbors	Interatomic distances, Å
Bi I	4a	0.108	0	0	7 Pd	2.93; 3.22; 2.96; 2.92; 2.92; 2.96; 2.96
					7 Bi	3.30; 3.55; 3.55; 3.76; 3.78; 3.78; 3.76
Pd I	4a	0.108	0	0.275	7 Bi	Coordinates of Pd relative to Bi the same as for Bi relative to Pd in the equivalent position
Bi II	4a	0.650	0	0	2 Pd	2.70; 2.70
					7 Pd	2.96; 2.90; 2.93; 2.92; 2.92; 2.96; 2.96
					7 Bi	3.30; 3.76; 3.76; 3.78; 3.78; 3.78; 3.78
Pd II	4a	0.650	0	0.275	7 Bi	Coordinates of Pd relative to Bi the same as for Bi relative to Pd in the equivalent position
Bi III	8a	0.125	0.274	0.722	2 Pd	3.00; 3.00
					7 Pd	2.92; 2.95; 2.92; 2.96; 2.93; 3.00; 3.02
					8 Bi	3.55; 3.76; 3.78; 3.76; 3.76; 3.78; 3.62; 3.78
Pd III	8a	0.125	0.274	0.447	7 Bi	Coordinates of Pd relative to Bi the same as for Bi relative to Pd in the equivalent position
					2 Pd	2.70; 3.00

CONCLUSION

The investigations carried out on alloys of bismuth with palladium have confirmed our previous tentative fusion diagram for the bismuth-palladium system. The position of the liquidus curve in the fusion diagram has been established, and the melting temperatures of the phases in the system have been determined with greater accuracy. In the concentration interval ~43–54% by weight Pd, the existence of a solid solution region analogous to the region in the antimony-palladium system has been confirmed.

The variation of the X-ray pattern with varying heat treatment of the alloy observed by the authors of Ref. 11 in their X-ray investigation of differently heat-treated alloys of composition corresponding to Pd_5Bi_3 (45.9% by weight Pd) has been interpreted erroneously. What these authors describe as the high-temperature modification of a compound Pd_5Bi_3 is in reality the γ -phase, which has a considerable range of solubility. The hexagonal cell with $a = 4.50$ and $c/a = 1.29$ cited by the authors is

actually a pseudo-cell; owing to the presence of the super-lattice the true cell occupies a volume three times as large. What is referred to as the low-temperature modification of the compound Pd_5Bi_3 is really the product of the eutectoid decomposition of the γ -phase, consisting of a mixture of crystals of the two compounds BiPd and Bi_2Pd . The data obtained for this system indicate that superconductivity is manifested by compounds possessing extremely diverse types of crystal lattices, even including structures having no center of symmetry, as, for example, BiPd.⁸

TABLE 5

Compound	Minimum interatomic distances, Å			
	<i>T_c</i>	Bi – Pd	Bi – Bi	Pd – Pd
α - Bi_2Pd	1.7	2.78	3.29	2.78
BiPd	3.7	2.92	3.30	2.70
β - Bi_2Pd	4.25	2.97	3.36	3.36

Analysis of the interatomic distances and comparison of these with the temperatures of the transitions to the superfluid state (Table 5) indicates that increase in the minimum interatomic distances in superconducting bismuth-palladium compounds leads to an increase in T_c .

I would like to take this opportunity to express my indebtedness to Prof. G. S. Zhdanov for his valued advice and instruction in the fulfillment of the present work.

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