

## The Structure of Superconductors VIII. X-ray and Metallographic Investigations of the System Bismuth - Rhodium.

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The system Bi-Rh has been investigated metallographically and by x-rays and has been found to contain three compounds: BiRh, Bi<sub>2</sub>Rh in two modifications, and Bi<sub>4</sub>Rh in three modifications. Crystals have been obtained and the primitive cell and space group determined for α-Bi<sub>4</sub>Rh and the primitive cell for α- and β-Bi<sub>2</sub>Rh.

THE structural diagram of the system bismuth-rhodium (Fig. 1) has been determined by

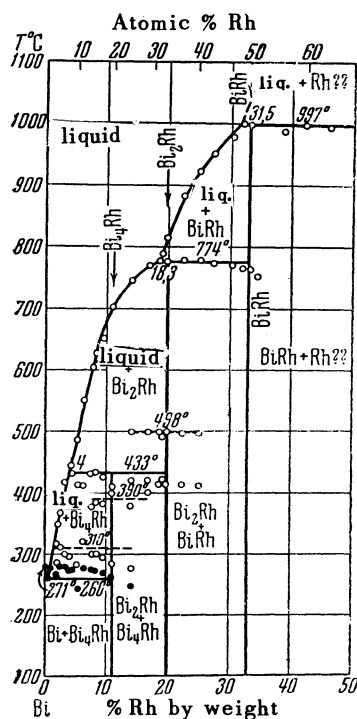


Fig. 1. Diagram of the System Bi - Rh

Rode<sup>1</sup> on the basis of thermal and metallographic analysis.

According to the findings of Alekseevskii<sup>2</sup>, all compounds in this system (Bi<sub>4</sub>Rh, Bi<sub>2</sub>Rh and BiRh) can be obtained in the superconducting

state. However a series of essential questions has remained obscure. The majority of alloys having the compositions Bi<sub>2</sub>Rh and Bi<sub>4</sub>Rh had superconducting transition temperatures  $T_k$  in the vicinity of 3.4° K. In some cases alloys of composition Bi<sub>4</sub>Rh passed into the superconducting state at temperatures in the neighborhood of 2.9° K. For a series of specimens of Bi<sub>4</sub>Rh it was possible to observe both transition points to the superconducting state. After annealing, alloys of composition Bi<sub>4</sub>Rh and Bi<sub>2</sub>Rh lost the capability of becoming superconducting while annealed alloys of composition BiRh preserved this capability. The temperature  $T_k$  for annealed as well as for unannealed alloys of composition BiRh lies in the vicinity of 2° K, although the transition temperature in various specimens varies within a range of several tenths of a degree. These small fluctuations, as has been shown by the work of one of us with Glagoleva<sup>3</sup>, can be explained by small changes in phase composition under annealing, since BiRh constitutes a phase of variable composition. The clarification of the other points mentioned above required a deeper investigation of this system and the employment of both metallographic methods of inquiry, x-ray methods of analysis as well as measurement of micro-hardness and, in individual cases, of the density of compounds.

**Preparation of Alloys.** Bismuth of purity 99.95% and rhodium of analytical purity (domestic sources) were employed for the preparation of the alloys. Part of the alloys were prepared in the laboratory of N. E. Alekseevskii at the Institute for Physical Problems of the Academy of Sciences, USSR, and part in the laboratory of the Moscow In-

<sup>1</sup>E. J. Rode, Communications of the Platinum Institute 7, 21 (1929)

<sup>2</sup>N. E. Alekseevskii, n. V. Brandt and T. I. Kostina, Izv. Akad. Nauk SSSR, Phys. Ser. 16, 233 (1952)

<sup>3</sup>V. P. Glagoleva and G. S. Zhdanov, J. Exper. Theoret. Phys. USSR 25, 485 (1953)

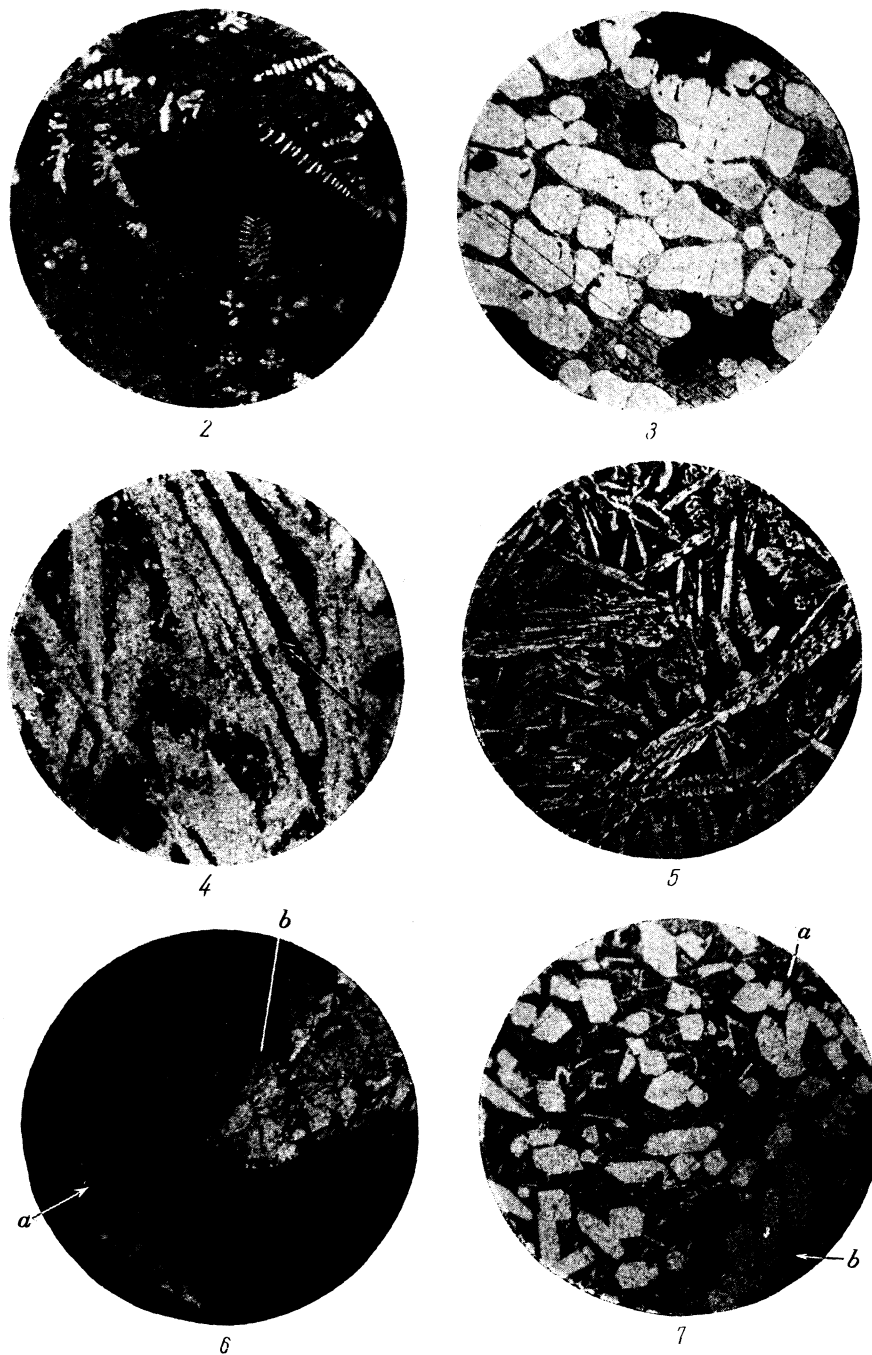


Fig. 2. 43% Rh by wt. Etched by concentrated  $\text{HNO}_3$ . Magnification 134.  
 Fig. 3. 70% Rh by wt. Etched by concentrated  $\text{HNO}_3$ . Magnification 57.  
 Fig. 4. 11.01% Rh by wt. Etched by  $\text{KI} + \text{I}$ . Magnification 57.  
 Fig. 5. 3.5% Rh by wt. Etched by  $\text{KI} + \text{I}$ . Magnification 57.  
 Fig. 6. Surface of laminar and needle shaped crystals. Magnification 57.  
 Fig. 7. 3.5% Rh by wt. Etched by  $\text{KI} + \text{I}$ . Magnification 134.

stitute for Engineering Physics. Melting was carried out in an atmosphere of inert gas (helium, argon) in sealed quartz ampules in a high frequency furnace, in a resistance furnace and in a gas jet flame.

The alloying of bismuth with rhodium was carried out in various proportions by weight. Annealed alloys were investigated as well as those quenched at various temperatures and at various rates of cooling.

**Microstructure.** For the preparation of section slides alloys were poured over sulphur or over a special cement. A solution of iodine in potassium iodide was employed as an etching agent for metallographic analysis principally for alloys with a large content of bismuth, and nitric acid and aqua regia were employed for alloys rich in rhodium.

The microstructures which we observed in the region from approximately pure bismuth to 50%rhodium by weight were similar to those adduced in reference 1.

Alloys rich in rhodium, which were not investigated by Rode, show a double phased structure. Alloys ranging from the compound  $\text{BiRh}$  to pure rhodium consist of a mixture of crystals of  $\text{BiRh}$  in rhodium, the number of rhodium crystals increasing with the rise in the total content of rhodium in the alloy. Rhodium can crystallize in the form of dendrites (Fig. 2) as well as in single crystals of irregular shape (Fig. 3). X-raygrams taken by using x-radiation from copper on alloys rich in rhodium support the metallographic observations.

Precise x-raygrams were obtained from alloys which were rich in rhodium and which were annealed for 50 hours at a temperature of  $1100^\circ\text{C}$ , using x-radiation from copper in an RKU camera of diameter 114 mm. These x-raygrams were used to determine the lattice period of rhodium crystals in the alloy. Within the limits of experimental error the magnitude of this period coincides with the period of pure rhodium, a result which indicates the negligible solubility of bismuth in rhodium in contrast to our findings of significant solubility of bismuth<sup>4</sup>, as well as of antimony and lead<sup>5</sup> in palladium. It is interesting to note that while rhodium and palladium have the same crystal structure, comparable lattice parameters and atomic radii, and are neighbors in the Periodic Table, they behave differently with respect to solubility of bismuth. Doubtless this result is connected with

the differences in the electronic structures of the atoms of rhodium and palladium and shows the inadequacy of purely geometrical investigations of solid solutions, an inadequacy one often finds in the metallographic literature.

#### THE COMPOUND $\text{Bi}_4\text{Rh}$ AND ITS POLYMORPHIC MODIFICATIONS

Alloys corresponding to the composition  $\text{Bi}_4\text{Rh}$  (11.01% Rh by weight), under customary conditions of cooling, turn out to be heterogeneous as a consequence of the incompleteness of the peritectic reaction. Sections obtained from such alloys show the existence of several phases. On the microphotograph of Fig. 4 there are seen initial separations of  $\text{Bi}_2\text{Rh}$  which did not succeed in reacting with the liquid alloy, and which appear as gray dendrites surrounded by a later growth of a thin (1-10  $\mu$ ) film of crystals of  $\text{Bi}_4\text{Rh}$  (shown by the arrow in the Figure). The dark etched places correspond to the eutectic which is composed principally of bismuth (99.3% by weight). In all probability, the film of  $\text{Bi}_4\text{Rh}$  obstructs the entry of crystals of  $\text{Bi}_2\text{Rh}$  into reaction with the bismuth of the eutectic. Continued heating at a temperature sufficient for the conduct of a process of diffusion between the bismuth of the eutectic and  $\text{Bi}_2\text{Rh}$  permits the reaction to go to completion, resulting in the formation of the low-temperature modification of  $\text{Bi}_4\text{Rh}$ . According to the observations of Alekseevskii<sup>2</sup>, and our findings, this temperature lies above  $100^\circ\text{C}$ . A heterogeneous alloy of  $\text{Bi}_4\text{Rh}$  annealed for 16 hours at a temperature of  $200^\circ\text{C}$ , after annealing, showed a uniform structure under metallographic and x-ray analysis. Alloys obtained through different rates of cooling differ with respect to the number of phases.

A powder x-raygram obtained from a conventionally cooled specimen shows, on a strong background, many weak lines which are hard to measure. The interpretation of this x-raygram is extremely intricate, since all three phases have complex structures with a large number of superimposed lines. In addition to the large number of lines and their superpositions, there is involved the effect of line diffusion, ensuing from the smallness of the crystals of  $\text{Bi}_4\text{Rh}$  and from stresses.

As noted by Rode, a well defined temperature pause occurs in the alloy at the temperature  $\sim 310^\circ$ , and a weakly defined one at the temperature  $\sim 390^\circ$ ; these correspond, according to Rode's surmise, to polymorphic transformations of  $\text{Bi}_4\text{Rh}$ .

Investigations by Alekseevskii<sup>2</sup> on the super-

<sup>4</sup>N. N. Zhuravlev and G. S. Zhdanov, J. Exper. Theoret. Phys. USSR 25, 485 (1953)

<sup>5</sup>M. Hansen, *The Structure of Binary Alloys* (1941)

conducting properties of alloys of this composition showed that only the unannealed specimens passed into the superconducting state thus indicating the presence of polymorphic transformations. We made an attempt to obtain a high temperature modification of  $\text{Bi}_4\text{Rh}$  by way of quenching, in water at  $20^\circ\text{C}$  and in ethyl alcohol at  $-55^\circ\text{C}$ , crystals of the low temperature modification of  $\text{Bi}_4\text{Rh}$  heated to various temperatures from  $300^\circ$  to  $430^\circ\text{C}$ . This attempt did not lead to the expected results.

It is interesting to note that x-raygrams taken from quenched crystals had clearer lines than those taken from crystals separated from annealed alloys. This fact is indicative of the relaxation of stresses in the crystals. It was decided to obtain quenched crystals of  $\text{Bi}_4\text{Rh}$  by separation from the alloy ingot. To this end, an alloy containing 3.5% by weight of Rh was used on the basis that, irrespective of the rapidity of cooling of such an alloy from a temperature slightly ( $10-20^\circ$ ) lower than the melting point of  $\text{Bi}_4\text{Rh}$  ( $433^\circ$ ), a two-phase alloy would be formed consisting of the eutectic and crystals of  $\text{Bi}_4\text{Rh}$ . Such an alloy was obtained. Figure 5 is a microphotograph showing crystals of  $\text{Bi}_4\text{Rh}$  imbedded in a mass of eutectic. Crystals of  $\text{Bi}_4\text{Rh}$  were separated in the form of a black powder by dissolving the bismuth in dilute nitric acid. From the powder x-raygram of the crystals separated in this way it is difficult to judge the crystal structure, since the photographs show weak lines on a strong background. Evidently the cause of this appearance of the x-raygrams is tied to the smallness of the crystals ( $1-25\mu$  as determined from the microphotographs) and the magnitude of the stresses in the crystals, both of which lead to strong diffusion of lines.

Crystals of larger size were obtained from a later melt, which was cooled less rapidly. Crystals of  $\text{Bi}_4\text{Rh}$ , separated by the process of dissolving bismuth in dilute nitric acid, had dominantly needle shaped forms, a fact which has also been noted by Rossler (see reference 5). In the mass of needle shaped crystals there were also observed single crystals in the form of thin laminas. Observation of the needle shaped crystals under a microscope disclosed growths of needles in the form of "brooms", growths in the form of packets of crystals, as well as single needles. Cross sections of needle shaped crystals are rectangular or close thereto.

In the microphotograph shown in Fig. 6, the arrow *a* points to a packet growth of crystals of  $\text{Bi}_4\text{Rh}$ ; the rectangularity of the crystal cross sections can also be seen. Probably these crys-

tals are associated with one of the orthogonal systems. Microscopic investigation of the laminar crystals shows that they are of a character significantly different from the needle shaped ones and probably belong to a third modification of  $\text{Bi}_4\text{Rh}$ . Arrow *b* in Fig. 6 shows a laminar crystal whose plane lies in the plane of the microphotograph. It is interesting to point out that on the laminar crystals which have been studied, cleavage lines can clearly be observed inclined at angles of approximately  $120^\circ$ . This fact allows the presumption that these crystals belong to the hexagonal system with the hexagonal axis being located at right angles to the plane of the lamina.

The discovery of three habit forms for the crystals of  $\text{Bi}_4\text{Rh}$  underlies the possibility of the existence of three modifications of the compound  $\text{Bi}_4\text{Rh}$  which we will call  $\alpha$  (low temperature),  $\beta$  (needle shaped) and  $\gamma$  (laminar). Modifications  $\beta$ - $\text{Bi}_4\text{Rh}$  and  $\gamma$ - $\text{Bi}_4\text{Rh}$  can be obtained by rapid cooling from temperatures in the interval  $310-390^\circ$  for  $\beta$ - $\text{Bi}_4\text{Rh}$  (in accord with the structural diagram) and in the interval  $390-433^\circ$  for  $\gamma$ - $\text{Bi}_4\text{Rh}$ . The quenching temperatures must be reached by cooling the alloy from a temperature higher than the melting point of  $\text{Bi}_4\text{Rh}$  ( $433^\circ$ ), this being essential if crystals of the  $\alpha$ -modification are to be eliminated.

Crystals obtained from an alloy of composition 3.5% by weight of rhodium, and quenched at a temperature of  $350^\circ\text{C}$ , had primarily the needle shaped form and represented  $\beta$ - $\text{Bi}_4\text{Rh}$ . Crystals obtained from an alloy of the same composition, but quenched at a temperature of  $420^\circ\text{C}$ , had primarily laminar form and represented  $\gamma$ - $\text{Bi}_4\text{Rh}$ . In Fig. 7 a microphotograph is shown of an alloy of composition 3.5% rhodium by weight, quenched at a temperature of  $350^\circ\text{C}$ , in which the needle shaped crystals can be seen in cross section (arrow *a*) among the mass of eutectic and, in small amount, the laminar crystals (arrow *b*).

As mentioned previously, attempts to obtain the modifications  $\beta$  and  $\gamma$ - $\text{Bi}_4\text{Rh}$  by annealing crystals of  $\alpha$ - $\text{Bi}_4\text{Rh}$  in the intervals of temperatures  $310-390^\circ$  and  $390-433^\circ$ , and by subsequent quenching in water and in ethyl alcohol, did not succeed. Experiments were also made to obtain these modifications by way of annealing and quenching heterogeneous alloys containing bismuth along with  $\alpha$ - $\text{Bi}_4\text{Rh}$ . Heterogeneous alloys were obtained of compositions 3.5 and 9% rhodium by weight, containing the eutectic and crystals of  $\alpha$ - $\text{Bi}_4\text{Rh}$ ; these alloys were heated in argon

filled glass ampules up to the temperature 400-420°C and held for 3-6 hours, after which they were quickly cooled in water. After such quenching the alloy became very friable; it was possible to separate single crystals from it by mechanical means. By measurement of microhardness, and checking by x-ray analysis, it was established that these crystals represent  $\alpha\text{-Bi}_4\text{Rh}$ . The friability of bismuth attests to the great rapidity of cooling, which it was not possible to obtain in cooling alloys in quartz ampules. It is interesting to note that alloys of composition 3.5% rhodium by weight, cooled from higher temperature, broke up into powder as if disintegrating. The quenching of pure bismuth at the temperature 700°C produced this effect and could evidently be explained by the increase in volume of bismuth on crystallization. Accordingly, to obtain high temperature modifications of  $\text{Bi}_4\text{Rh}$  from crystals of  $\alpha\text{-Bi}_4\text{Rh}$ , it is probably essential that a prolonged period of time be allowed for the conduct of the process of diffusion through which these modifications are produced. The reverse diffusion process for the passage of high temperature modifications of  $\text{Bi}_4\text{Rh}$  into  $\alpha\text{-Bi}_4\text{Rh}$ , as was mentioned previously, takes place at temperatures exceeding 100°C.

Powder x-raygrams of the three modifications, obtained on irradiation by  $K\alpha$ -copper, have distinct dispositions of lines pointing to the existence of distinct crystalline structures.

#### THE PRODUCTION OF CRYSTALS AND STRUCTURAL STUDIES OF THE MODIFICATION $\alpha\text{-Bi}_4\text{Rh}$ .

Crystals of  $\alpha\text{-Bi}_4\text{Rh}$  were obtained by growth in the mother liquor and subsequent separation by way of dissolving the bismuth. An alloy consisting of 3% rhodium by weight was chosen which, with appropriate heat treatment, contained the eutectic and crystals of  $\alpha\text{-Bi}_4\text{Rh}$ . The alloy was prepared in a quartz ampule containing argon. Melting was carried out in a resistance furnace. The temperature of the furnace was carried to 650-700°C, the rhodium dissolved in the bismuth, and the furnace was slowly cooled to a temperature of 350-400°C. The alloy was held at this temperature for two hours (in order that the reaction might be fully completed) and was then cooled to room temperature, together with the furnace. Phase composition was checked by metallographic analysis. If the existence of two phases was detected the alloy was annealed at 300-350°C for 20-40 hours. As a result of such heat treatment there were formed large crystals of  $\alpha\text{-Bi}_4\text{Rh}$  with linear sections of

0.3-0.5 mm. In Fig. 8 there is shown a microphotograph of such an alloy; on the dark background of the etched eutectic are seen the bright crystals  $\alpha\text{-Bi}_4\text{Rh}$ . The crystals of  $\alpha\text{-Bi}_4\text{Rh}$  were separated from the alloy by dissolving the bismuth in 25% nitric acid. The crystals of  $\alpha\text{-Bi}_4\text{Rh}$  are silver-gray in color, crystallize in polyhedral shapes, the faces of which give good optical reflections. The more perfect of the separated crystals were chosen for x-ray structural studies. It was established by Laue diagrams that the crystals belong to the cubic system and the diffraction class  $O_h = m\bar{3}m$ , and by vibration x-raygrams that the crystals have a body-centered unit cell with the period  $a = 14.9 \pm 0.2 \text{ \AA}$ . After greater precision was attained by the method of Umanskii and Kvitka<sup>6</sup> through the reflection of 1860 at the angle  $78^\circ 59'$  from the radiation of copper in a camera of diameter 144.4 mm, it was found that

$$a = 14.928 \pm 0.005 \text{ \AA}.$$

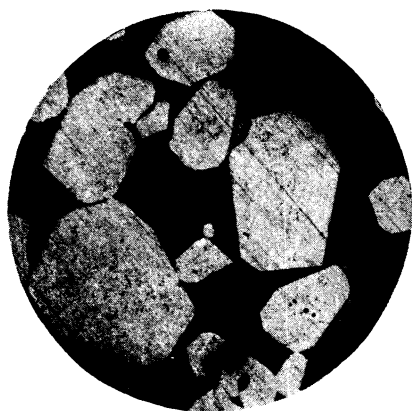
X-ray density  $\sigma_x = 11.24 \text{ gm/cm}^3$ . The unit cell contains 24 weight units which corresponds to 120 atoms of bismuth and rhodium. As a result of the indications of the series of vibration and rotation x-raygrams the extinction law was established, and from this followed x-ray group No. 115<sup>7</sup>, containing the single-space group  $O_h^{10} - Ia\bar{3}d$ .

#### THE COMPOUND $\text{Bi}_2\text{Rh}$ AND ITS POLYMORPHIC MODIFICATIONS

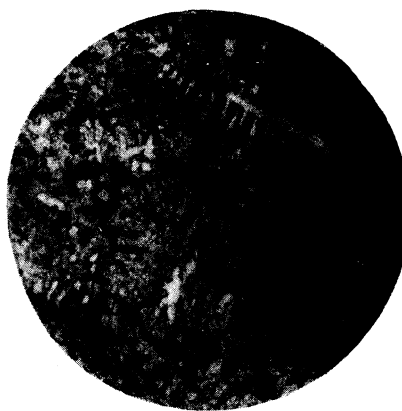
According to the structural diagram (Fig. 1) the compound  $\text{Bi}_2\text{Rh}$  is formed by a peritectic reaction. Conventionally cooled alloys turn out to be heterogeneous as a consequence of the incompleteness of the peritectic reaction. Alloys obtained by different rates of cooling differ with respect to the number of phases. In such alloys the fundamental phase is the high temperature modification  $\beta\text{-Bi}_2\text{Rh}$ , with small quantities of  $\text{Bi}_4\text{Rh}$ , and, occasionally, bismuth and  $\text{BiRh}$ . Figure 9 shows a microphotograph of a conventionally cooled alloy where the basic gray mass consists of  $\beta\text{-Bi}_2\text{Rh}$ , the bright dendrites are  $\text{BiRh}$ , and the strongly etched dark places are  $\text{Bi}_4\text{Rh}$ . A powder x-raygram obtained from such an alloy shows, on a strong background, many weak lines which are difficult to measure.

<sup>6</sup>M. M. Umanskii and S. S. Kvitka, Izv. Akad. Nauk SSSR, Phys. Ser. 15, 153 (1953)

<sup>7</sup>G. S. Zhdanov and V. A. Pospelov, J. Exper. Theoret. Phys. USSR 15, 709 (1945)



8



9



10



11



a



b

12

- Fig. 8. 3% Rh by wt. Etched by KI + I. Magnification 57.  
Fig. 9. 19.81% Rh by wt. Etched by concentrated  $\text{HNO}_3$ . Magnification 255.  
Fig. 10. 17% Rh by wt. Etched by 35%  $\text{HNO}_3$ . Magnification 57.  
Fig. 11. Section of a high temperature modification. Magnification 57.  
Fig. 12. Surface of the alloy 21.5% Rh by wt. Magnification 55.

Crystals were obtained of the low and high temperature modifications of Bi<sub>2</sub>Rh. To obtain  $\alpha$ -Bi<sub>2</sub>Rh an alloy containing 17% by weight of rhodium was employed. The alloy was prepared in a quartz ampule in an atmosphere of argon. Melting was carried out in a resistance furnace. The temperature of the furnace was carried to 900-1000°C, the rhodium dissolved in bismuth, and the furnace was slowly cooled to a temperature of 450-480°C. The alloy was held at this temperature for 15-20 hours, after which it was cooled together with the furnace. In Fig. 10 is presented a microphotograph of such an alloy in which the large light crystals are those of  $\alpha$ -Bi<sub>2</sub>Rh and the etched places, Bi<sub>4</sub>Rh and bismuth. Crystals of  $\alpha$ -Bi<sub>2</sub>Rh were separated from the alloy by dissolving the Bi<sub>2</sub>Rh and bismuth in 35% nitric acid at 40-50°C. Crystals of  $\alpha$ -Bi<sub>2</sub>Rh had laminar form, were of a dull gray color, and the faces were not reflecting. Powder x-raygrams of such crystals show the presence of many clear lines. Through a preliminary structural x-ray study, carried out with a monocrystalline growth, it is possible to assign the crystal  $\alpha$ -Bi<sub>2</sub>Rh to the rhombic system with the periods:

$$a = 5.9 \pm 0.3 \text{ \AA}, b = 6.8 \pm 0.3 \text{ \AA}, c = 7.2 \pm 0.3 \text{ \AA}.$$

The elementary cell contains 4 parts by weight, that is, 12 atoms.

Alloys containing the high temperature modification of Bi<sub>2</sub>Rh have a flaky character. From ingots of the alloy it is possible to split off mechanically very thin (several hundredths of a millimeter) laminas with good optical reflections. Figure 11 shows a microphotograph of a split from such an alloy. In spite of the great care which was used, it was not possible to separate, by mechanical means, crystals of  $\beta$ -Bi<sub>2</sub>Rh which would be useful for x-ray study, because the laminas were too easily deformed during the separation. In order to obtain underformed crystals of  $\beta$ -Bi<sub>2</sub>Rh, alloys were employed whose composition was richer in bismuth than would correspond to stoichiometric proportions. As was mentioned previously, such alloys, under rapid cooling, are characterized by reticular and needle shaped structures of crystals of  $\beta$ -Bi<sub>2</sub>Rh surrounded by thin layers of crystals of Bi<sub>4</sub>Rh<sup>2</sup> (Fig. 5). In the spaces between crystals the lattice is filled with bismuth. The thickness of the layers of crystals of Bi<sub>4</sub>Rh depends on the rapidity of cooling of the alloys. Crystals of  $\beta$ -Bi<sub>2</sub>Rh were separated by dissolving bismuth and Bi<sub>4</sub>Rh in dilute nitric acid.

According to the structural diagram, and as was shown above, the compound Bi<sub>2</sub>Rh can exist in two modifications:  $\alpha$ -Bi<sub>2</sub>Rh formed as a result of slow cooling of the alloys and  $\beta$ -Bi<sub>2</sub>Rh obtained as a result of rapid cooling of the alloys. The passage of the crystals of  $\beta$ -Bi<sub>2</sub>Rh into  $\alpha$ -Bi<sub>2</sub>Rh takes place comparatively rapidly under annealing of the crystals of  $\beta$ -Bi<sub>2</sub>Rh at temperatures not exceeding 498°C. The reverse passage of  $\alpha$ -Bi<sub>2</sub>Rh into  $\beta$ -Bi<sub>2</sub>Rh requires more prolonged annealing in the temperature interval 498-774°C. Probably  $\beta$ -Bi<sub>2</sub>Rh exists in some region of concentrations. The variation in microhardness of the crystals of  $\alpha$ -Bi<sub>2</sub>Rh in various alloys over a wide range (70-330 kg<sup>2</sup>/mm<sup>2</sup>) can be explained in the light of this fact.

Co-crystallization of the two modifications of Bi<sub>2</sub>Rh was observed by us on the surface of ingots of the alloy containing a shortage of rhodium in proportion to the stoichiometric composition of Bi<sub>2</sub>Rh. If we exclude the effect of differences in the rate of cooling in various parts of the alloy, then the co-crystallization can be viewed as an indication of the difference in the composition of the different modifications. Figure 12 shows a microphotograph of the surface of an alloy containing 21.5% by weight of rhodium in which the large dark rhombic crystals correspond to  $\alpha$ -Bi<sub>2</sub>Rh (probably  $\alpha$ -Bi<sub>2</sub>Rh crystallizes in the form of rhombic bipyramids) while the light laminar crystals correspond to  $\beta$ -Bi<sub>2</sub>Rh. There were also observed a small quantity of the dendrites of BiRh shown by the arrow in Fig. 12b.

#### THE COMPOSITION BiRh

Investigation of phase composition in the region of the compound BiRh supports the structural diagram of Rode. Facts about the solubility of bismuth in BiRh and the crystal structure of BiRh were published in reference 3.

#### DENSITY AND MICROHARDNESS OF COMPOUNDS

Table I lists the densities  $\sigma_x$  calculated from the results of x-ray analysis and  $\sigma_{\text{hydr}}$  determined by hydrostatic weighing in carbon tetrachloride of the crystals of Bi<sub>4</sub>Rh and Bi<sub>2</sub>Rh. The density of BiRh is reduced from the data of Glagoleva and Zhdanov<sup>3</sup>.

Microhardness of the compounds was measured on the apparatus PMT-3 with a constant loading of 10 gms on the indenter. Measurements were carried out on crystals in the alloys as well as on crystals separated from the alloys and in an isolated state. Measurements were made on several specimens from

TABLE I

Compound	At Room Temperature gms/cm <sup>3</sup>	
	$\sigma_{\text{hydr}}$	$\sigma_x$
$\alpha$ -Bi <sub>4</sub> Rh . . . . .	11.0	11.24
$\beta$ -Bi <sub>4</sub> Rh . . . . .	10.7	—
$\gamma$ -Bi <sub>4</sub> Rh . . . . .	10.7	—
$\alpha$ -Bi <sub>2</sub> Rh . . . . .	12.2	12
$\beta$ -Bi <sub>2</sub> Rh . . . . .	11.4	11.6
BiRh . . . . .	12.5	12.65

various alloys and the results were averaged. The conditions of measurement and the preparation of the surfaces of the specimens were the same within practical limits.

Table II lists the mean microhardness and the limits of its variation for isolated crystals of the compounds.

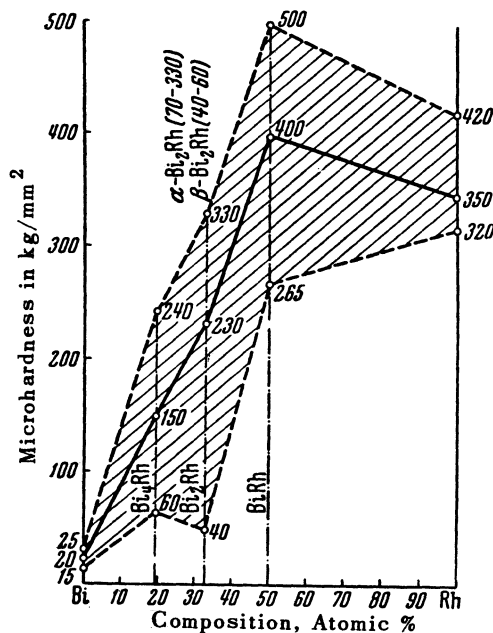


Fig. 13. Plot of the microhardness of crystals of compounds in the alloy.

In Fig. 13 is given a plot of the microhardness of compounds in the system bismuth-rhodium; the thick line gives the mean microhardness, while the dashed line gives the limits of variation of the microhardness, which fall within the limits of accuracy of the measurements. The results can be explained in a number of ways:

TABLE II

Compound	Mean micro-hardness in kg/mm <sup>2</sup>	Limits of variation of micro-hardness
$\alpha$ -Bi <sub>4</sub> Rh . . . . .	105	95—115
$\beta$ -Bi <sub>4</sub> Rh . . . . .	65	60—70
$\gamma$ -Bi <sub>4</sub> Rh . . . . .	40*	30—55
$\alpha$ -Bi <sub>2</sub> Rh . . . . .	230	210—260
$\beta$ -Bi <sub>2</sub> Rh . . . . .	45	40—50
BiRh . . . . .	410	370—450

\* Measured with a load of 5 gms on the indentor.

1) for the compound BiRh the small range of hardness may be explained by the solubility of bismuth in BiRh<sup>3</sup>;

2) for Bi<sub>2</sub>Rh and Bi<sub>4</sub>Rh it is necessary to take into account the existence of several modifications with different hardness, as well as the effect of the size of crystals in the alloy; moreover, for Bi<sub>2</sub>Rh the possibility of the existence in the compound of some homogeneous region is not to be excluded;

3) the microhardness of rhodium is measured on crystals of rhodium in alloys rich in rhodium; the range of microhardness can be explained by the effect of crystal size.

Figure 13 shows that in the system bismuth-rhodium the mean microhardness of the compounds increases with a rise in the content of rhodium, and that the microhardness of the compound (BiRh) rich in rhodium is greater than the microhardness of crystals of rhodium in the alloy. Similarly to the microhardness, there can be noted the increase in density of the low temperature modifications of the compounds with an increase in their rhodium content.

## CONCLUSIONS

1. In the system bismuth-rhodium the existence of three compounds is confirmed: Bi<sub>4</sub>Rh, Bi<sub>2</sub>Rh and BiRh.
2. The compound Bi<sub>4</sub>Rh has three modifications:  $\alpha$  (low temperature) — with crystals in the form of polyhedra,  $\beta$  (medium temperature) — with needle shaped crystals and  $\gamma$  (high temperature) — with lamellar crystals.  
 $\alpha$ -Bi<sub>4</sub>Rh crystallizes in the cubic system with the period  $a = 14.928 \pm 0.005 \text{ \AA}$ . The elementary cell contains 24 parts by weight, which corresponds to 120 atoms;  $\sigma_x = 11.24 \text{ gm/cm}^3$ . The space



group is  $O_h^{10} - Ia3d$ . By habit the crystals of  $\beta\text{-Bi}_4\text{Rh}$  belong to the orthogonal system, while those of  $\gamma\text{-Bi}_4\text{Rh}$  belong to the hexagonal system.

3. The compound  $\text{Bi}_2\text{Rh}$  has two modifications:  $\alpha$  (low temperature) and  $\beta$  (high temperature).

$\alpha\text{-Bi}_2\text{Rh}$  crystallizes in the rhombic system:  $a = 5.9 \pm 0.3 \text{ \AA}$ ;  $b = 6.8 \pm 0.3 \text{ \AA}$ ;  $c = 7.2 \pm 0.3 \text{ \AA}$ .

In the elementary cell there are four parts by weight, or 12 atoms:  $\sigma_x = 12.1 \text{ gm/cm}^3$ ;  $\beta\text{-Bi}_2\text{Rh}$  crystallizes in the monoclinic system:  $a = 16.2$

$\pm 0.1 \text{ \AA}$ ;  $b = 7.0 \pm 0.1 \text{ \AA}$ ;  $c = 10.3 \pm 0.1 \text{ \AA}$ ;  $\beta = 92^\circ 30'$ . In the elementary cell there are 16 parts by weight, or 48 atoms;  $\sigma_x = 11.6 \text{ gm/cm}^3$  (see Supplement).

4. Alloys rich in rhodium have a two phase character consisting of  $\text{BiRh}$  and rhodium.

5. The solubility of bismuth in rhodium is very slight and cannot be shown by x-ray analysis.

6. The density and microhardness of compounds in the system bismuth-rhodium have been determined.

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### SUPPLEMENT

#### THE X-RAY DETERMINATION OF THE ELEMENTARY CELL OF $\beta\text{-Bi}_2\text{Rh}$ .

Crystals of  $\beta\text{-Bi}_2\text{Rh}$  constitute thin laminas with two reflecting faces. Through a Laue diagram the crystals of  $\beta\text{-Bi}_2\text{Rh}$  was placed in the monoclinic system. The period along the monoclinic axis  $b$ , lying in the plane of the lamina, was obtained by a rotation x-raygram,  $b = 7.0 \pm 0.1 \text{ \AA}$ . The periods  $a$ ,  $c$  and the angle between them, were determined from the evolvment of three layer lines from an x-ray goniometer with a cylindrical film while the crystal was rotated about the axis  $b$ . It was found:

$$a = 16.2 \pm 0.1 \text{ \AA}; c = 10.5 \pm 0.1 \text{ \AA}; \beta = 92^\circ 30''$$

X-ray density  $\sigma_x = 11.6 \text{ gm/cm}^3$ , with the number of parts by weight per unit cell being  $Z = 16$ , corresponding to 48 atoms.

Translated by N. E. Golovin  
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## The Problem of the Superconductivity of the Compounds $\text{Bi}_4\text{Rh}$ and $\text{Bi}_2\text{Rh}$

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The temperature of transition into the superconducting state of the crystals of  $\beta$  and  $\alpha\text{-Bi}_4\text{Rh}$  are determined. An explanation is given of unstable behavior of the superconducting alloys of bismuth with rhodium.

As reported earlier<sup>1</sup>, alloys of composition  $\text{Bi}_4\text{Rh}$  and  $\text{Bi}_2\text{Rh}$  show superconductivity when they have not been annealed, and have transition temperatures, independent of composition, lying in the vicinity of  $2.9^\circ$  and  $3.4^\circ \text{K}$ . Specimens of the same composition which have been annealed do not show superconductivity. In order that the specimens may again become superconducting, it is necessary to remelt them. It was also noted that the majority of specimens of  $\text{Bi}_4\text{Rh}$  and  $\text{Bi}_2\text{Rh}$ ,

after the second remelting, gave a transition temperature in the neighborhood of  $3.4^\circ \text{K}$ . In the case of several specimens of alloys of composition  $\text{Bi}_4\text{Rh}$ , it was possible to observe a discontinuity in the critical field curve corresponding to the existence of two points of transition into the superconducting state from  $T_k = 3.4$  and  $T_k = 2.9^\circ \text{K}$ .

The fact that, after annealing, specimens lost the capacity of becoming superconducting was considered to be indicative of the existence of superconducting high temperature modifications of the compound  $\text{Bi}_2\text{Rh}$  and  $\text{Bi}_4\text{Rh}$ . The disappearance of superconductivity in annealed speci-

<sup>1</sup> N. E. Alekseevskii, N. B. Brandt and T. I. Kostina, *Izv. Akad. Nauk SSSR Ser. Fiz.* **16**, 233 (1952)