

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 Bi_2Rh has two modifications: α (low temperature) and β (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 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.

We express deep gratitude to Prof. N. E. Alekseevskii and to V. P. Glagoleva for productive collaboration and for joint discussion of the results of the work. We also express thanks to I. I. Lifanov and N. P. Ivanova, E. I. Michurina and

N. S. Senjeiko for assistance in the preparation of alloys, preparation of x-raygrams and microsections.

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
33

The Problem of the Superconductivity of the Compounds Bi_4Rh and Bi_2Rh

N. E. ALEKSEEVSKII, G. S. ZHDANOV AND N. N. ZHURAVLEV
The Institute for Physical Problems of the Academy of Sciences, USSR

The Moscow Institute of Engineering Physics

(Submitted to JETP editor February 24, 1954)

J. Exper. Theoret. Phys. USSR **28**, 237-240 (February, 1955)

The temperature of transition into the superconducting state of the crystals of β 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 earlier¹, alloys of composition Bi_4Rh and Bi_2Rh show superconductivity when they have not been annealed, and have transition temperatures, independent of composition, lying in the vicinity of 2.9° and 3.4°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 Bi_4Rh and Bi_2Rh ,

after the second remelting, gave a transition temperature in the neighborhood of 3.4°K . In the case of several specimens of alloys of composition Bi_4Rh , 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 Bi_2Rh and Bi_4Rh . The disappearance of superconductivity in annealed speci-

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

mens is explained by the polymorphic transformation of the modifications mentioned above.

The loss of superconductivity after annealing at temperatures slightly above 100°C, as well as the sharp change in the coefficient of expansion in the temperature interval 100-120°C, which was discovered during dilatometric measurements of two specimens of Bi₄Rh*, give some indication of the presence of polymorphic transformations in this temperature region.

Metallographic and x-raygraphic investigations² of alloys in the neighborhood of compositions

Bi₄Rh and Bi₂Rh were confirmed by the existence of several modifications of these compounds with points of polymorphic transition in agreement with the structural diagram of this system first investigated by Rode³. Investigation of the compound Bi₄Rh showed that it can be obtained in three modifications: α -Bi₄Rh-low temperature, β -Bi₄Rh-middle temperature, and γ -Bi₄Rh-high temperature form.

Crystals of α -Bi₄Rh (separated from annealed alloys with 3% by weight of rhodium) crystallize into the cubic system with the period $a = 14.928 \pm 0.005 \text{ \AA}$. The elementary cell contains 24 parts by weight, or 120 atoms of rhodium and bismuth; $\sigma_x = 11.24 \text{ gm/cm}^3$. The space group is $O_h^{10} - Ia\bar{3}d$. The α modification of Bi₄Rh does not become superconducting down to the temperature 0.1°K⁴. Crystals of β -Bi₄Rh separated from an alloy containing 3.5% of rhodium by weight, and quenched at a temperature of 300°-390°C, pass into the superconducting state at the temperature $T = 3.2^\circ\text{K}$. Crystals of γ -Bi₄Rh separated from the same alloy and quenched from a temperature close to the melting point of this compound, show superconductivity at $T = 2.7^\circ\text{K}$.

The transition temperatures of specimens previously observed at 3.4° and 2.9°K obviously were determined by the presence in them of the β and γ phases. The higher T_k of these specimens (in comparison with the T_k of the pure phases) most probably can be explained either by the partial solution of other components of the alloy in the superconducting compound, or by the great internal stresses arising in a heterogeneous

specimen.

The compound Bi₂Rh can be obtained in two modifications: α -Bi₂Rh-low temperature and β -Bi₂Rh-the high temperature form. Crystals of α -Bi₂Rh (separated from annealed alloys containing 17% of rhodium by weight) crystallize into the rhombic system with the periods $a = 5.9 \pm 0.34 \text{ \AA}$;

$b = 6.8 \pm 0.3 \text{ \AA}$ and $c = 7.2 \pm 0.3 \text{ \AA}$. The elementary cell contains 4 parts by weight, $\sigma_x = 12.1 \text{ gm/cm}^3$. Crystals of α -Bi₂Rh do not pass into the superconducting state down to the temperature 1.34°K. Crystals of β -Bi₂Rh, separated from an alloy containing 14 to 17% by weight of rhodium, quenched from a temperature close to the melting point of this compound, crystallize into the monoclinic system with the parameters $a = 16.2 \pm 0.1 \text{ \AA}$; $c = 10.5 \pm 0.1 \text{ \AA}$; $\beta = 92^\circ 30'$; $\sigma_x = 11.6 \text{ gm/cm}^3$. Crystals of β -Bi₂Rh also do not pass into the superconducting state down to the temperature 1.27°K.

In addition to the well-defined determination of the temperature of transition into the superconducting state, it is possible, in some degree, to explain the behavior of alloys obtained under various conditions and having the compositions Bi₂Rh and Bi₄Rh.

As has been shown in the work cited in references 1 and 2, alloys of composition Bi₄Rh cooled in the conventional way have a heterogeneous character. Depending on the rapidity of cooling, it is possible to observe in such alloys the presence of two modifications of Bi₂Rh and three modifications of Bi₄Rh. Annealing of alloys of composition Bi₄Rh at temperatures above 100°C leads to homogeneous structures. Moreover, the changes (loss of superconductivity, a sharp change in the coefficient of expansion) noted in the work of reference 1 under annealing above 100°C probably are better explained by the continuation of the peritectic reaction producing α -Bi₄Rh.

For specimens of composition Bi₄Rh there are possible five basic variants in the phase composition of the alloys, depending on the conditions of cooling.

First Variant. At rapid rates of cooling the reaction between crystals of Bi₂Rh and Bi does not go to completion. The speed of cooling is such that only the formation of γ -Bi₄Rh is possible. In such specimens there is only one transition point corresponding to γ -Bi₄Rh. To this variant corresponds specimen No. 1 and the specimen remelted after annealing No. 6¹.

On Fig. 1 is shown a microphotograph of an alloy of composition 9% rhodium by weight characterizing the first variant of phase composition. On the microphotograph can be seen bright crystals

² N. N. Zhuravlev and G. S. Zhdanov, J. Exper. Theoret. Phys. USSR 28, 228 (1951); Sov. Phys. 1, 91 (1955)

³ E. J. Rode, Communications of the Platinum Institute 7, 21 (1929)

⁴ N. E. Alekseevskii and Iu. P. Gaidukov, J. Exper. Theoret. Phys. USSR 25, 383 (1953)

* Dilatometric measurements were carried out in the laboratory of P. G. Strelkov.

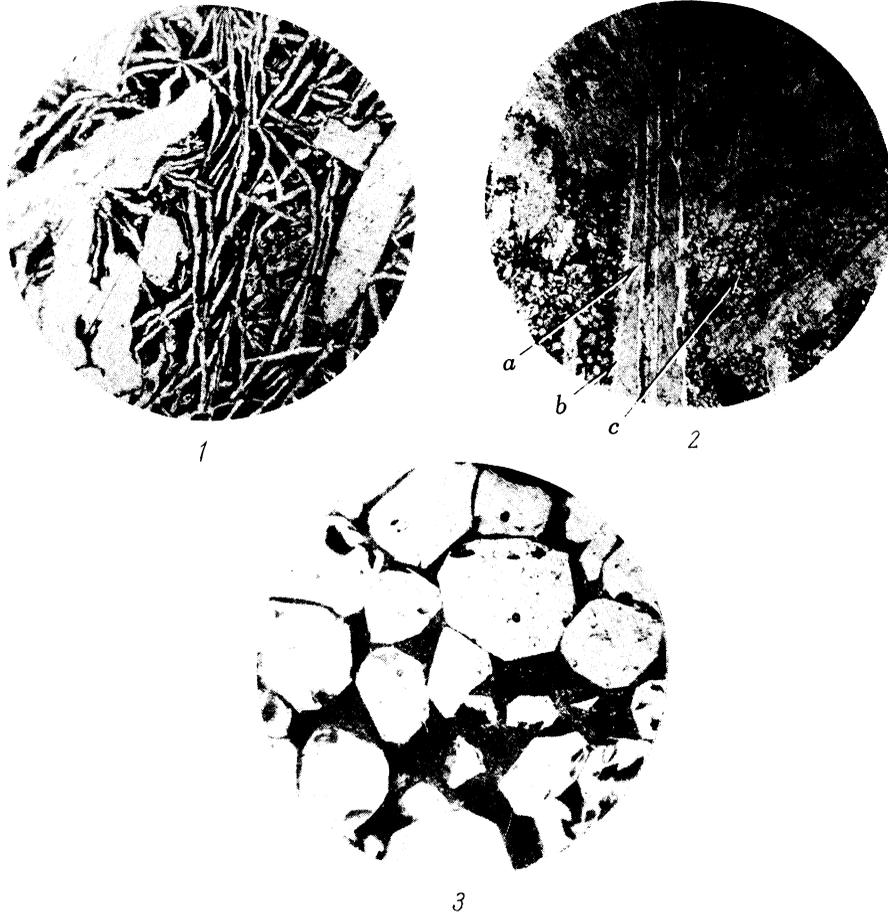


Fig. 1. Composition of 9% Rh by wt. Etched KI + I. Magnification 134.

Fig. 2. Composition of 11% Rh by wt. Etched KI + I. Magnification 57.

Fig. 3. Composition of 9% Rh by wt. Etched KI + I. Magnification 57.

surrounded by a film. The bright crystals represent $\beta\text{-Bi}_2\text{Rh}$ with a microhardness of 40-60 kg/mm^2 . The coating represents $\gamma\text{-Bi}_4\text{Rh}$ with a microhardness of 30-55 kg/mm^2 . The etched places correspond to the eutectic containing principally bismuth (99.3% by weight).

Second Variant. At rates of cooling slower than in the first case, the reactions between the crystals of Bi_2Rh and bismuth are carried out to a greater extent but are not completed; under such circumstances the formation of the modifications α , β and $\gamma\text{-Bi}_4\text{Rh}$ is possible. Such specimens have two points of transition into superconductivity corresponding to $T_k = 3.2^\circ\text{K}$ for $\beta\text{-Bi}_4\text{Rh}$ and $T_k = 2.7^\circ\text{K}$ for $\gamma\text{-Bi}_4\text{Rh}$. To this variant correspond samples No. 4 and No. 6 obtained in quartz ampules.

In Fig. 2 is shown a microphotograph of an alloy of composition 11% rhodium by weight, character-

izing the second variant of phase composition. On the microphotograph the long gray crystals represent $\beta\text{-Bi}_2\text{Rh}$ with a microhardness of 40-60 kg/mm^2 (shown by the arrow *a*). The lighter film of longish crystals with a microhardness of 30-55 kg/mm^2 represent $\gamma\text{-Bi}_4\text{Rh}$ (arrow *b*). The small four-sided crystals with a microhardness of 60-70 kg/mm^2 represent $\beta\text{-Bi}_4\text{Rh}$ (arrow *c*), the small polyhedral crystals $\alpha\text{-Bi}_4\text{Rh}$ with a microhardness of 90-200 kg/mm^2 (the upper limit of hardness is raised because of the influence of crystal size). The etched places are the bismuth of the eutectic.

Third Variant. The reaction between crystals of Bi_2Rh and bismuth has proceeded to completion. The speed of cooling is sufficient for the formation of crystals of β and $\gamma\text{-Bi}_4\text{Rh}$. Such specimens have two points of transition into the superconducting state corresponding to β and

γ -Bi₄Rh.

The metallographic picture is close to that shown in Fig. 2, the difference being merely that the longish crystals have smaller microhardness and lighter coloring. To differentiate between crystals of β -Bi₄Rh and γ -Bi₄Rh is difficult since they look similar on microsections and have similar values of the microhardness. In a heterogeneous alloy it is not possible to do this even by x-ray analysis. This variant of phase composition is observed in cases in which the alloy is heated to a temperature higher than the melting temperature of Bi₄Rh by 150-200°C, and is then cooled to a temperature a little lower than the melting point of Bi₄Rh, is held at this temperature for some time sufficient for the reaction between Bi₂Rh and bismuth to be completed, and is then rapidly cooled.

Fourth Variant. The reaction between the crystals of Bi₂Rh and the bismuth of the eutectic has run to completion. The speed of cooling suffices for the formation of crystals of β -Bi₄Rh, but is not sufficient for the formation of γ -Bi₄Rh. In such specimens there is only one transition point corresponding to β -Bi₄Rh. Specimen No. 2, melted in a thick-walled quartz ampule, corresponds to this variant, and specimens No. 8 and 9 prepared in graphite crucibles.

Fifth Variant. The reaction between crystals of Bi₂Rh and the bismuth of the eutectic has run to completion. The speed of cooling is too small for the formation of crystals of β and γ -Bi₄Rh. The specimens are not superconducting. As an example,

we have specimen No. 7 which was melted in a thick-walled porcelain container. In Fig. 3 is shown a microphotograph of an alloy of composition 9% rhodium by weight, characterizing the fifth variant of phase composition. In the microphotograph, in the mass of etched eutectic, can be seen bright polyhedral crystals of α -Bi₄Rh with a microhardness of 90-120 kg/mm².

Similar to the alloys of composition Bi₄Rh, the alloys of composition Bi₂Rh, when conventionally cooled, also have a heterogeneous character. It is sufficient to point out that under various conditions of preparation of the alloys, in addition to the modifications mentioned above, at very rapid rates of cooling, it is possible to form crystals of Bi₂Rh which can give one more point of transition into superconductivity $\sim 2^\circ\text{K}$, as was mentioned in reference 5. Alloys of composition Bi₂Rh obtained by us through conventional cooling, as was mentioned above, had heterogeneous character and consisted primarily of crystals of Bi₂Rh and β -Bi₄Rh. The latter were responsible for the superconductivity of these alloys. As examples, can serve specimen No. 1 melted in a quartz ampule, and specimens No. 3 and No. 4 melted in graphite crucibles.

In conclusion we express thanks to I. I. Lifanov and to N. P. Ivanov for assistance in the experiments.

⁵N. E. Alekseevskii, N. B. Brandt and T. I. Kostina, J. Exper. Theoret. Phys. USSR 21, 951 (1951)

Translated by N. E. Golovin