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SOVIET PHYSICS JETP VOLUME 34(7), NUMBER 4 OCTOBER, 1958

STRUCTURE OF SUPERCONDUCTORS: XII
INVESTIGATION OF BISMUTH — RUBIDIUM ALLOYS

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A provisional melting diagram is constructed for the Bi — Rb system on the basis of thermal, microscopic, and x-ray data. Four compounds have been established for the Bi — Rb system: Bi_2Rb, $BiRb_3$, and two others which presumably are Bi_2Rb_3 and $BiRb_2$. The superconducting compound Bi_2Rb crystallizes in the cubic system with a lattice constant a = 9.609 A and has a structure of the Cu_2Mg type.

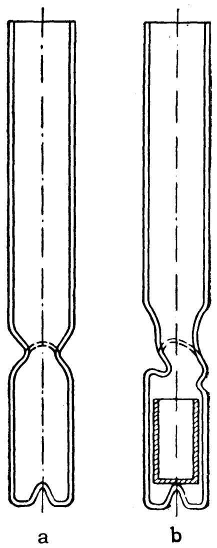
According to data obtained by Alekseevskii,[1] heterogeneous alloys of bismuth with rubidium, having a large excess of bismuth, go over into the superconducting state at a temperature of 4.25°K. In spite of the non-uniformity of the alloys, the curves showing the superconducting transition displayed relatively little scatter, thus indicating the existence of a superconducting bismuth — rubidium compound. One of the purposes of the present investigation was to ascertain the composition and the atomic-crystalline structure of this compound.

The study of the bismuth — rubidium system involved the solution of a series of experimental problems. The principal difficulties were conditioned by the large chemical activity of metallic rubidium and by the markedly different physiochemical natures of bismuth and rubidium. All the investigations were carried out with a small quantity of rubidium (~ 3 gm), so that we had to develop micromethods for preparing the alloys and for analyzing them physiochemically. A certain quantity of metallic rubidium was obtained by one of the authors from the vacuum reduction of rubidium — iodide by calcium.[2]

PREPARATION OF THE ALLOYS

The large chemical activity of metallic rubidium required the creation of conditions which would prevent the oxidation of the metal during the process of preparing a charge, putting it into an iron crucible or a quartz capsule, and melting it. The methods of preparing alloys which are described in the literature relate principally to the less active alkali metals — lithium, sodium, and potassium, and were designed to be used for the separate melting of comparatively large quantities of metal, of the order of several grams or more. Our attempts to find methods described in the literature for preparing small quantities of bismuth — rubidium alloys (of the order of tenths of grams) gave no positive results. After an entire series of experiments carried out by one of the authors,[3] we arrived at the following method of preparing the alloys. A special pipette was made from a quartz tube (Fig. 1).

FIG. 1.


a

b

FIG. 2.

Liquid rubidium was drawn into the volume A, which was terminated at both ends by capillaries. After the rubidium had hardened, the pipette was weighed on an analytical balance and the weight of rubidium was determined from the difference in the weights of the pipette with and without the rubidium. In such a pipette the surface area of the rubidium in contact with the atmosphere was small (the capillary diameter was 0.2 — 0.6 mm). The loss of rubidium during the time necessary to prepare a charge (2 — 3 minutes) was negligible. The error in the determination of the composition of an alloy did not exceed 0.1%. A known weight of bismuth was placed in the quartz capsule, or into an iron crucible placed in the quartz capsule (Fig. 2a, b). By means of a specially-made apparatus the rubidium, under a pressure of helium, was run off into the quartz capsule or into the iron crucible located in the capsule, and the capsule was removed.

A diagram of the apparatus used for fusing the rubidium and sealing off the capsule is shown in Fig. 3. The whole assembly is fastened to a common laboratory stand 1. The brass capsule holder 3 is made fast to the pillar of the stand by means of a sleeve 2. The quartz capsule 4 with the iron crucible 5, in which there is a known weight of bismuth, is connected to the holder through a length of vacuum hose 6. The pipette 19 containing the rubidium projects down into the capsule through a hole in the center of the holder, which is sealed off by means of a rubber packing 7, a collar 8, and a nut 9. The lower end of the pipette (the capillary) leads into the iron crucible. The upper end is connected through a piece of vacuum hose 10 to a forepump and to a helium cylinder 11. The capsule holder is attached to the forepump through a connecting pipe 12. Valves 13 and 14 are opened, and the air is pumped out of the capsule and the pipette. Then valves 13 and 14 are closed and helium from the cylinder is let into the upper end of the pipette through valve 15. The rubidium is melted with the aid of a resistance oven 16 and flows into the crucible under the pressure of the helium gas. The pipette is carefully raised upward so that its lower end is beyond the vicinity of the capsule neck 17. The lower end of the capsule, containing the charge, is wrapped with wet cotton wads and the capsule is sealed off at the neck with

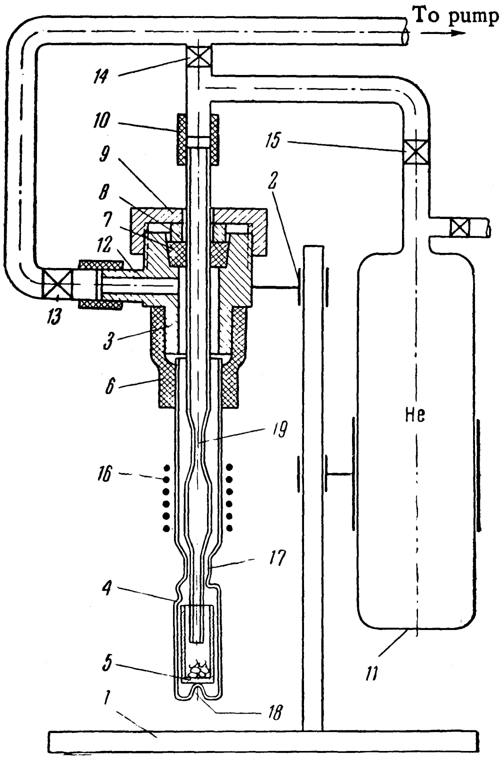


FIG. 3. Arrangement of the apparatus for fusing the rubidium and sealing off the capsule.

the flame of an oxygen torch. An indentation 18 is provided in the capsule for the insertion of a thermocouple junction.

Chemically pure bismuth and rubidium with a calcium impurity of about 3% were used for preparing most of the alloys. Some of the alloys were made with chemically pure rubidium and bismuth. Within the limits of error of the experiment, no appreciable difference was observed between the alloys of bismuth with pure rubidium and with rubidium containing a calcium impurity.

The melting was carried out in a small-gauge resistance oven specially constructed for the purpose. For the alloys containing small amounts of rubidium, quartz capsules of small volume (2 — 5 cm^3) were used for melting the samples and for recording their cooling curves. The alloys containing large amounts of rubidium were melted in iron crucibles placed inside the small-volume quartz capsules. The recording was carried out inside the capsules as follows. The capsule with its iron crucible was placed in the oven and the charge was melted down in the crucible. Then, after the alloy had soaked, the oven was turned over so that the alloy could run into the end of the capsule, where there was an indentation provided for a thermocouple, and the cooling curve was recorded. The preparation directly in the capsule of alloys with a large rubidium content led to a change in the composition of the alloy, since at high temperatures rubidium reacts with the surface of the quartz; a layer is formed thereby which inhibits the further loss of rubidium from the alloy. The preliminary alloying of bismuth with rubidium in the iron crucibles with the subsequent recording of cooling and heating curves inside the quartz capsules makes it possible to obtain alloys with a composition practically corresponding to that of the given charge.

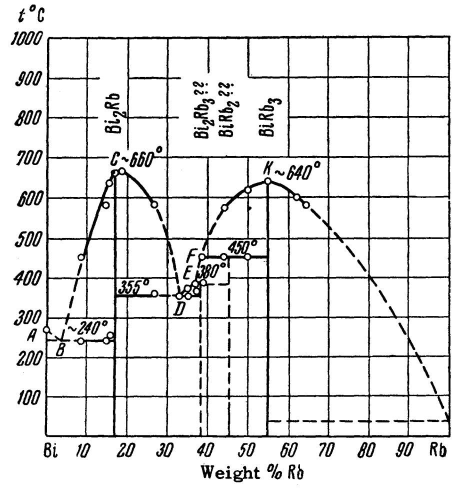


FIG. 4. Melting diagram of the Bi-Rb system.

THERMAL ANALYSIS OF THE ALLOYS

Heating and cooling curves were recorded with an electronic automatic potentiometer EPP-09 down to a temperature of 50 — 100°C. The weight of the alloys varied from 0.3 to 1 gm. The results obtained from the thermal analysis are displayed graphically in Fig. 4.

The melting temperature of bismuth with rubidium added decreases along the line AB down to ~ 240 — 250°C. A eutectic point lies at about 2 — 4% by weight Rb. From the eutectic point the melting curve gradually increases along the line BC, reaching a maximum at ~ 660°C at point C for 17% by weight Rb, which corresponds to the compound Bi_2Rb. A further addition of rubidium is accompanied by a falling melting curve, and on the cooling curves a eutectic stop occurs at ~ 355 — 360°C. An increase in the rubidium content of the alloy leads to a rising melting curve along the line DEFK. At the point K the curve achieves a maximum at ~ 640°C for an alloy of composition 55% by weight Rb, corresponding to the compound $BiRb_3$. Alloys in the range of compositions from the eutectic point D up to the point K revealed temperature stops at ~ 380° and ~ 450°C. The presence of these stops permits us to consider the possibility that two compounds, presumably Bi_2Rb_3 and $BiRb_2$, crystallize out in a peritectic reaction. From the point K on, the melting curve falls as the rubidium content increases.

MICROSCOPIC INVESTIGATION OF THE ALLOYS

A metallographic study was carried out for alloys rich in bismuth with compositions up to that of Bi_2Rb. This study showed that as the rubidium content of the metal increases, the number of crystals of the compound Bi_2Rb increases. In Fig. 5a, b are shown microphotographs of alloys with rubidium contents of 9 and 15% by weight, in which the dark etched spots are crystals of Bi_2Rb, and the light field is the eutectic Bi + Bi_2Rb. As can be seen from the microphotographs, alloys with 15.8% by weight Rb, which are close in composition to the compound Bi_2Rb (17% by weight), contain a small amount of eutectic and are almost homogeneous. Since the preparation of microsections of alloys enriched with rubidium presented experimental difficulties, we studied cross-sections of the alloys microscopically at magnifications of 35, 70, and 120. The phases in the bismuth — rubidium system differed in color. This difference made it possible to estimate the phase composition of an

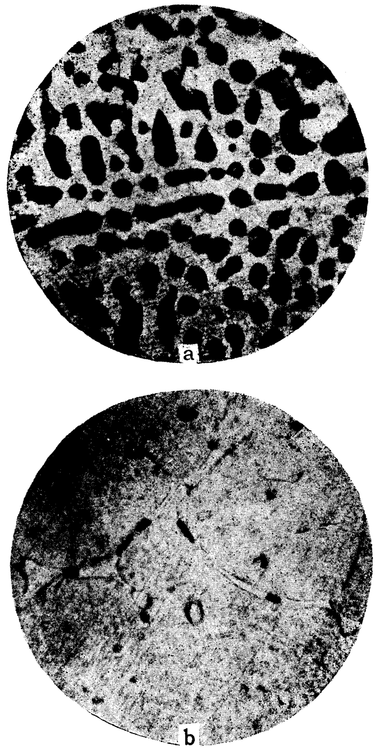


FIG. 5. a) etched with HCl, magnified 200×, b) etched with HCl, magnified 200×.

alloy from its cross-section. Such microscopic studies of the phase composition of alloys rich in rubidium supported the data obtained by thermal analysis.

DETERMINATION OF THE STRUCTURE OF THE SUPERCONDUCTING COMPOUND Bi_2Rb

A comparison of the results of the present investigation with data from low temperature measurements on alloys rich in bismuth 1 shows that the compound Bi_2Rb is a superconductor. An x-ray study of this compound was carried out to determine its atomic structure. This investigation was complicated by the chemical activity of the alloy and by the difficulty of obtaining an alloy of a uniform stoichiometric composition from the alloying of small quantities of charge. At the end of a long experimental program, several satisfactory x-ray photographs were obtained which were of use in determining the structure of the compound Bi_2Rb.

The samples to be used for x-ray photographs were prepared in the following way. A bead of the alloy was crushed up in kerosene which had first been treated with sodium (by maintaining it at a temperature of 110 — 130°C and stirring it for 2 hours, and then filtering it). The alloy powder in the kerosene was drawn into a piece of quartz capillary, and the open end of the capillary was sealed with picein.

Using $CuK\alpha$ radiation and a RKU-86 camera, we obtained x-ray photographs of alloys with compositions close to that of Bi_2Rb (15.8%, 16.6%, etc.). Alloys with such compositions consist mostly of crystals of the compound Bi_2Rb and a small amount of the eutectic Bi + Bi_2Rb. Bismuth gives a large number of lines in x-ray powder patterns. In order to separate the bismuth lines from the compound lines in the x-ray photographs, we used a different size of crystal of Bi_2Rb and bismuth (the crystals of bismuth in the eutectic were considerably small then the crystals of the principal phase, Bi_2Rb). While the x-ray film was being exposed, the sample was rotated, but not with the customary large velocity; it performed only one or two revolutions during the whole time of exposure. As a result of such a process it was easy to separate the weak diffusion lines of the bismuth from the punctuated lines of the compound. The slow rotation of the sample was necessary in order that the points on the lines would be nearly in position and would permit the line intensities to be estimated. From x-ray diagrams obtained with a stationary sample it was difficult to estimate not only intensities of the lines but their location on the diagram as well.

From the x-ray powder patterns of the alloys, the intensities I and the displacements of the lines were measured, and the values of the interplanar distances d were calculated. All the lines of the x-ray photographs of Bi_2Rb crystals are indexed in the cubic system. Laue patterns obtained from single crystals of Bi_2Rb also served to assign these crystals to the cubic system.

The single crystals of Bi_2Rb were separated by mechanical means from alloys composed of 25% by weight Rb. During the exposure the crystal was immersed in a cellulose-nitrate varnish; consequently the surface of the crystal was covered with a thin film of the product of the interaction between the rubidium and the varnish. The Laue patterns were obtained with hard radiation (tungsten). Attempts to obtain x-ray patterns of the waves with copper radiation gave no positive results, and molybdenum radiation is unsuitable, since it gives a strong background due to the excitation of the L-series of bismuth.

The value $a = 9.590 \pm 0.002$ kX is obtained as the result of an accurate determination of the period of the Bi_2Rb cell. Calculations of the interplanar distances using this figure agree well with the measured values.

The most probable type of structure for Bi_2Rb is that of Cu_2Mg,[4] since the compound Bi_2K of

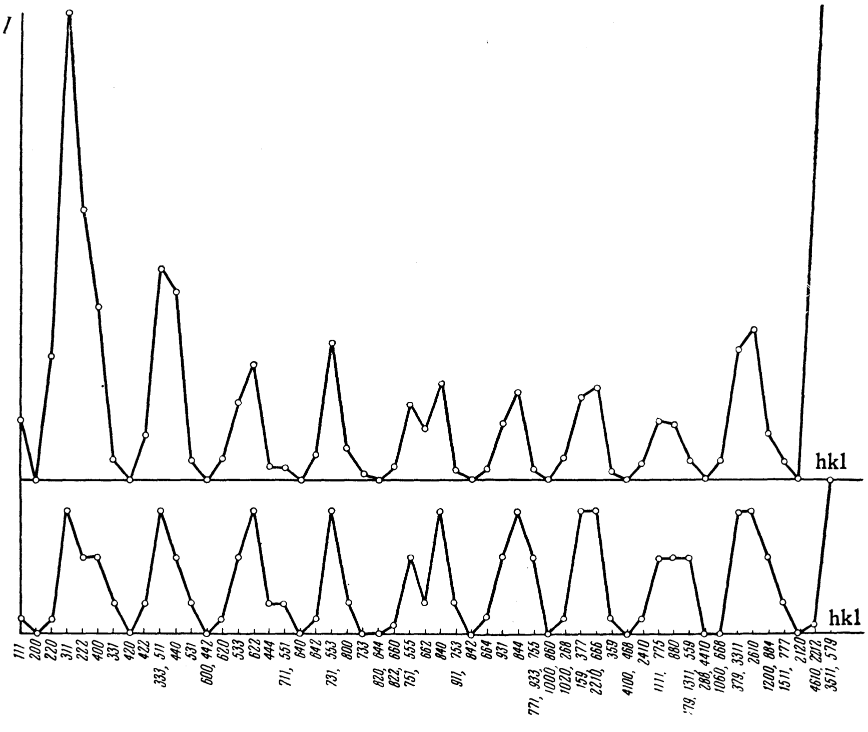


FIG. 6. Curves of I_{exper}(below) and I_{theoret}(above) for Bi_2Rb.

bismuth with calcium — the chemical analog of rubidium — crystallizes in a structure of the Cu_2Mg type[5] and its cell has a cubic parameter a close to that for the Bi_2Rb cell. The results of the indexing and a comparison of x-ray photographs of Bi_2K and Bi_2Rb reveal their similarity and show that these compounds are isomorphs. Using the method of hydrostatic suspension[6] in kerosene and carbon tetrachloride, we measured the density of an alloy with a 16.6% rubidium content, which is close to that of Bi_2Rb (17% by weight Rb), and found it to be equal to 7.1 gm/cm³. In the first approximation the density of this alloy can be taken to be the pycnometric density of Bi_2Rb crystals.

For $Z = 8$ we obtain $\sigma_X = 7.54$ gm/cm³. In a structure of the Cu_2Mg type the atoms occupy positions a and d (space group O_h^7 — Fd3m):

$$\text{Rb } 8(a): 0\ \ 0\ 0 \ldots\ldots$$
$$\text{Bi } 16(d): \frac{5}{8}\frac{5}{8}\frac{5}{8} \ldots\ldots$$

For the structural amplitudes:

$$\begin{aligned} F_{hkl} &= f_{\text{Rb}} \cos 2\pi \frac{h-k}{4} \cos 2\pi \frac{k-l}{4} \\ &\times \cos 2\pi \frac{l-h}{4} \cos 2\pi \frac{h+k+l}{8} \\ &+ f_{\text{Bi}} \cos 2\pi \frac{h-k}{4} \cos 2\pi \frac{k-l}{4} \cos 2\pi \frac{l-h}{4} \\ &\times \Big\{ \cos 2\pi \frac{h+k+l}{8} \cos 2\pi \frac{5}{8} h \cos 2\pi \frac{5}{8} k \cos 2\pi \frac{5}{8} l \\ &- \sin 2\pi \frac{h+k+l}{8} \sin 2\pi \frac{5}{8} h \sin 2\pi \frac{5}{8} k \sin 2\pi \frac{5}{8} l \Big\}. \end{aligned}$$

The line intensities were calculated from the formula

$$I \sim L_p p F^2,$$

where L_p is the Lorentz factor or the polarization and p is the recurrence factor. Comparison of the calculated and the measured intensities (Fig. 6) shows good agreement and supports the assignment of a structure of the Cu_2Mg type to crystals of Bi_2Rb.

The rubidium atoms in the Bi_2Rb structure are situated according to the diamond law.

In each empty octant, a regular tetrahedron of bismuth atoms is located in such a way that the edges of the small tetrahedron are parallel to the edges of a large one of rubidium atoms, and the center of gravity of the small tetrahedrons is located at the center of the octant. Each atom of rubidium is surrounded by 12 atoms of bismuth at distances of 3.98 A and by 4 atoms of rubidium at distances of 4.16 A. Each atom of bismuth has as nearest neighbors 6 atoms of bismuth at distances of 3.40 A and 6 atoms of rubidium at distances of 3.98 A.

CONCLUSIONS

1. A provisional melting diagram of the bismuth — rubidium system has been constructed.

2. The existence of four compounds in the bismuth — rubidium system has been discovered: Bi_2Rb, $BiRb_3$, and two compounds which presumably are Bi_2Rb_3 and $BiRb_2$. The compounds Bi_2Rb and $BiRb_3$ correspond to maxima on the melting diagram. In the alloying of the components these compounds are formed with a large evolution of

heat. The other two compounds are formed in a peritectic reaction.

3. The superconducting compound Bi_2Rb crystallizes in the cubic system with $a = 9.590 \pm 0.002$ kX and has a structure of the Cu_2Mg type.

4. An increase of the minimum interatomic spacing in Bi_2Rb relative to the isomorphic compound Bi_2K (Ref. 5) leads to an increase of the superconducting transition temperature from 3.58°K up to 4.25°K, analogous to the increase in T_c observed with increasing interatomic distances for compounds of bismuth with palladium,[8,9] rhodium, and nickel.[10]

In conclusion we express our thanks to Professor N. E. Alekseevskii for valuable advice during the performance of the present research and to R. N. Kuz' min for aid in carrying out the experiments.

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STRUCTURE OF SUPERCONDUCTORS: XIII

INVESTIGATION OF BISMUTH — CESIUM ALLOYS

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A provisional melting diagram is constructed for the Bi — Cs system. Three compounds were found: Bi_2Cs, $BiCs_3$, and one which probably is $BiCs_2$. The superconducting compound Bi_2Cs crystallizes in the cubic system with a lattice constant $a = 9.746 \pm 0.005$A and is isomorphic with the superconducting compounds Bi_2K and Bi_2Rb.

ACCORDING to experimental data,[1] certain bismuth — cesium alloys become superconductors at $T_c = 4.75$°K. It is assumed that a bismuth — cesium compound which is rich in bismuth is responsible for the superconductivity of these alloys. The principal goal of the present study of bismuth — cesium alloys was to ascertain the composition and the atomic-crystalline structure of this compound.

The investigation of bismuth — cesium alloys was accompanied by certain difficulties connected with the large chemical activity of metallic cesium. Having located a small quantity of metallic cesium (~ 2 gm) we used the micromethods developed for an experimental study of bismuth — rubidium alloys[2] to prepare the samples and to analyze them physiochemically.