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Structure of Superconductors. XI Investigation of Alloys of Bismuth with Platinum, Ruthenium, Osmium and Iridium

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Two superconducting compounds, BiPt and Bi_2Pt, are crystallized in the bismuth–platinum system. The compound Bi_2Pt crystallizes in two modifications, α and β. The appearance and disappearance of superconductivity in alloys of composition corresponding to Bi_2Pt may be explained by the presence of the high-temperature modification β-Bi_2Pt in these alloys. Bismuth does not form compounds with ruthenium, osmium or iridium by direct alloying.

INVESTIGATION OF THE ALLOYS of bismuth with platinum, ruthenium, osmium and iridium has been undertaken in connection with the study of superconductivity. A number of alloys of bismuth with elements in group VIII of the Mendeleev table become superconductors at low temperatures.[1–6]

1. THE BISMUTH–PLATINUM SYSTEM

It is known from data in the literature[7] that the solidification point for bismuth is lowered by approximately 2° by the addition of 0.2 – 1% by weight of platinum. It is suggested that the eutectic point corresponds to a concentration of less than 0.2% platinum. It is also known that when bismuth is alloyed with platinum two compounds are formed: BiPt and Bi_2Pt. The first has a structure of the type of nickel arsenide, with constants $a = 4.20$A, $c/a = 1.32$ (Refs. 8 and 9); for the second a structure of the type of pyrites is specified, with a constant $a = 6.683 \pm 0.005$A (Ref. 10). According to the data of Ref. 11, the compound BiPt becomes superconducting at 1.21° K, while from the data of Ref. 4 the transition occurs at ~ 2.4° K.

Samples of composition corresponding to Bi_2Pt give in some cases $T_c = 0.15°$ K, while in other cases they have no superconducting properties at all.[4] It is of interest to investigate the reason for such behavior in these alloys at low temperatures.

Thermal Analysis

Chemically pure bismuth and platinum were used in the preparation of the alloys. Melting was conducted in a resistance oven, in quartz capsules under an argon atmosphere. The heating and cooling curves were recorded with the aid of an electronic automatic potentiometer EPP-09 to temperatures of 200 – 400° C. The weights of the alloys lay between 0.5 and 1.5 g. After one heating and cooling curve had been recorded, the quantity of one or the other component needed to give the desired composition was added and another recording was made. Curves were recorded over a certain concentration interval (10 – 20% by weight), and then, to avoid accumulation of errors in the composition, the alloy was replaced by a freshly-compounded mixture of bismuth and platinum.

The results of the thermal analysis are presented in Fig. 1.

According to the data of Ref. 7 the addition of platinum lowers the melting temperature of bismuth by ~ 2° K. The EPP-09 apparatus does not have sufficient sensitivity to record a change in temperature within one-degree limits. For this reason we have not investigated the hypoeutectic alloys thermally. In the fusion diagram the melting point of bismuth *A* and the eutectic point *B* are very close to one another; with the scale used they coincide. From the eutectic point (~ 0.2% Pt) the liquefaction curve rises progressively along *BC* and at ~ 29% by weight Pt reaches a transition point at ~ 660°; at this temperature the compound Bi_2Pt melts with decomposition. The next segment of the liquefaction curve *CDE* beginning at ~ 29% by weight Pt rises as the platinum content of the alloy increases and reaches a maximum at 48.3% by weight Pt, corresponding to the compound BiPt. On the heating and cooling curves for alloys in the interval 11 – 32% by weight Pt a thermal effect is observed at ~ 390° having a large hysteresis which for a cooling rate of 20 – 25°/min reaches more than 100°. The magnitude of the hysteresis falls with increasing Pt content and reaches 20° for a composition corresponding to Bi_2Pt.

It is of interest to note that this thermal effect is not observed for alloys with platinum contents

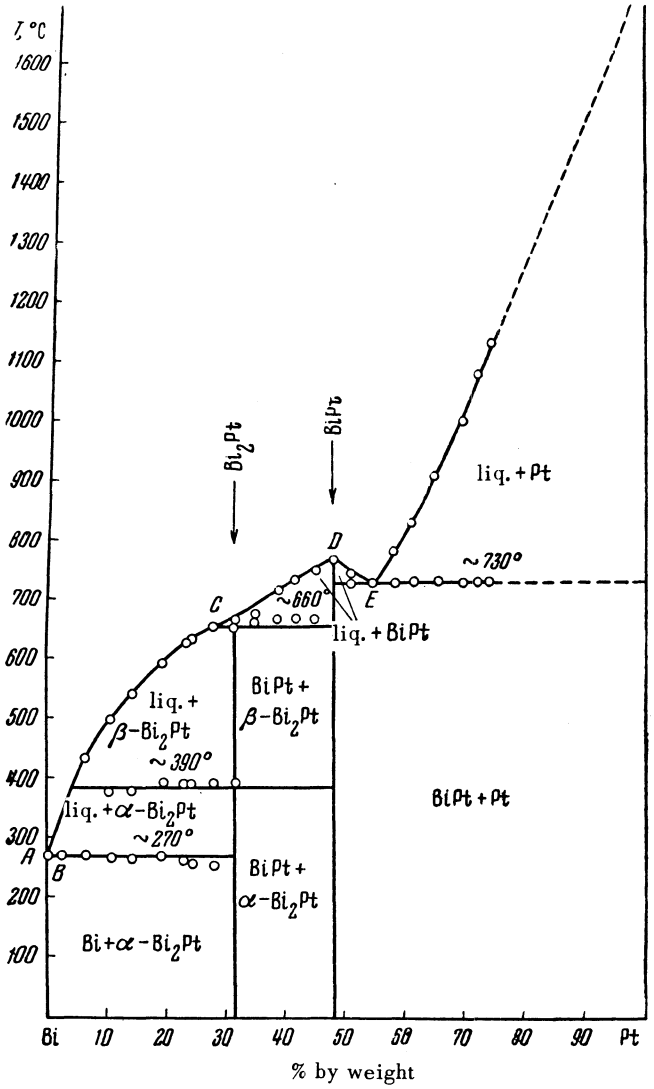

FIG. 1. Diagram of the Bi–Pt system

greater than that of the compound Bi_2Pt, although it should exist up to the concentration of BiPt. This can probably be explained by assuming that at these cooling rates the polymorphic transition does not take place in the solidified alloy. Further addition of platinum is accompanied by a fall in the liquefaction curve. Eutectic points are found on the cooling and heating curves at ~ 730°. From the point *E* onward the liquefaction curve rises steeply with increasing platinum content.

Microstructure and X-ray Phase Analysis

The investigation of the microstructure was carried out with alloys specially prepared for this purpose. In the study of the microstructure nitric acid and aqua regia were employed as etching agents. Alloys containing less than 31.84% by weight platinum consist of Bi_2Pt crystals and Bi_2Pt + Bi eutectic. The number of Bi_2Pt crystals precipitated increases as the platinum content rises. The compound Bi_2Pt crystallizes in two modifications with the temperature of the polymorphic transition ~ 390° Rapidly-cooled alloys in this composition interval at temperatures above 390° consist of eutectic and Bi_2Pt crystals of the high-temperature modification (β-Bi_2Pt), and annealed alloys of eutectic and Bi_2Pt crystals of the low-temperature modification (α-Bi_2Pt). Figure 2 shows a photomicrograph of an annealed alloy containing 8% by weight of platinum, in which light crystals of α-Bi_2Pt are visible in an

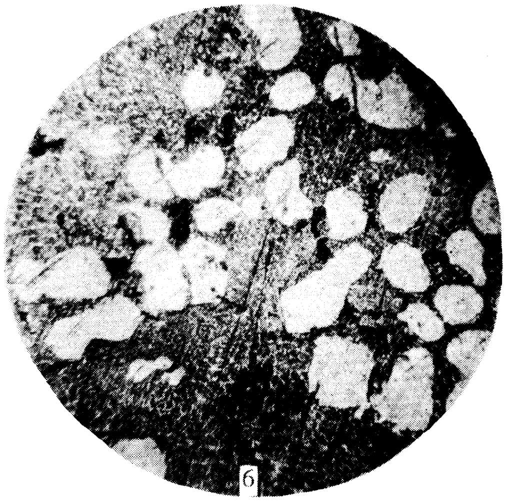

FIG. 2. Etched in HNO_3; magnification 86×.

FIG. 3. Etched in HNO_3; magnification 86×.

FIG. 4. Etched in HNO_3; magnification 201×.

FIG. 5. Etched in acid mixture (HNO_3 + HCl); magnification 440×.

FIG. 6. Etched in acid mixture (HNO_3 + HCl); magnification 200×.

FIG. 7. Etched in HNO_3; magnification 86×.

etched matrix of eutectic. Figure 3 shows a photomicrograph of a rapidly-cooled alloy of the same composition, in which needle-like (more probably tabular) crystals of β-Bi_2Pt can be seen in the etched eutectic matrix.

Alloys in the region between 31.8 and 48.3% by weight platinum are two-phase and consist of crystals of Bi_2Pt and of BiPt. Annealed alloys consist of crystals of α-Bi_2Pt and BiPt. Figure 4 shows a photomicrograph of an alloy containing 43% by weight of platinum, in which can be seen light BiPt crystals of irregular form and among them gray crystals of Bi_2Pt showing twinning lines similar to the lines observed for BiPd and Bi_2Pd.[12] The powder X-ray patterns obtained from annealed and rapidly-cooled alloys of the composition of BiPt (48.30% by weight Pt) are identical, which precludes polymorphism in this compound.

In alloys containing 48.3% by weight and higher of platinum, there is observed the formation of a BiPt + Pt eutectic (Fig. 5) with a eutectic point corresponding approximately to a concentration of 55% by weight platinum. Alloys more rich in platinum consist of crystals of platinum and BiPt + Pt eutectic. Figure 6 shows a photomicrograph of an alloy containing 70% by weight of platinum, in which light platinum crystals are visible in the eutectic matrix. A precision powder X-ray pattern was obtained, in a chamber 114 mm in diameter with radiations from copper, from platinum crystals separated from an alloy of this composition by dissolving the BiPt crystals in aqua regia. Calculation and indexing of the X-ray pattern showed that the magnitude of the lattice constant for the platinum crystals in the alloy agrees to within the limits of accuracy of the measurement with the constant for the initial pure platinum. This indicates a negligible solubility of bismuth in platinum, in contradistinction to the considerable solubility which we have found for bismuth in palladium,[12] as well as for antimony and lead[7] in palladium. Platinum, like rhodium,[13] does not dissolve bismuth.

Density and Micro-Hardness of the Compounds

The density σ_{hydr} of the compounds was determined with ingots weighing 0.5 – 1.5 g using the method of hydrostatic suspension[14] in carbon tetrachloride ($\sigma_{pycn} = 1.585$ gm/cm^3).

The densities σ_{hydr} and σ_X, the latter computed from X-ray data at room temperature, are listed in the table.

The micro-hardness of the compounds was measured in the PMT-3 apparatus, with a constant loading of 10 g on the indentor. Measurements were made on several samples from various melts, and the results were averaged. The average micro-hardness and its limits of dispersion are also listed in the table.

Production of β-Bi_2Pt Crystals

Two methods were employed to obtain β-Bi_2Pt crystals suitable for X-ray structural studies and investigation of superconducting properties: the method of production within a capillary, and the method of growth in a mother liquor. To obtain β-Bi_2Pt crystals using the first method an alloy was prepared whose composition corresponded closely to that of Bi_2Pt (31.84% by weight Pt). The alloy was placed within a quartz capsule terminating in a fine capillary (0.5 – 1 mm). The capsule was evacuated and placed within a tilting tubular resistance oven specially prepared for this purpose. The alloy was heated to 800 – 850° C, resulting in the formation of a droplet. The oven was swung into a vertical or inclined position, so that the droplet blocked the capillary. The tip of the capillary was wrapped in a dampened cotton pad (or immersed in water) and argon was admitted into the capsule; under this pressure the alloy filled the capillary, cooling rapidly. Using this method a number of β-Bi_2Pt samples were obtained in the form of aggregates of large crystals. These β-Bi_2Pt samples were not suitable for X-ray structural investigations, and were used in studying the superconducting properties.

In preparing crystals of β-Bi_2Pt by the second method alloys were employed having a composition richer in bismuth than that of Bi_2Pt. An alloy containing 8 – 10% by weight platinum was placed in a quartz capsule which was filled with argon. The alloy was heated to 700 – 750° and then cooled slowly to 420 – 450° C. The alloy was maintained at this latter temperature for several hours and then rapidly cooled. As a result of this heat treatment a two-phase alloy was obtained (Fig. 3) consisting of eutectic and deformed tabular crystals of β-Bi_2Pt. By selection of the rate of cooling for the alloy it proved possible to reduce the number of deformed β-Bi_2Pt crystals (Fig. 7).

The tabular β-Bi_2Pt crystals were separated from the alloy by dissolving the bismuth in dilute nitric acid. An interesting fact should be noted. If nitric acid of concentration greater than that necessary to dissolve the bismuth in the eutectic is used, not

Compound	σ_{hydr}, g/cm^3	σ_X, g/cm^3	Average micro-hardness, kg/mm^2	Limits of variation in micro-hardness
α—Bi_2Pt	13.3	13.6	145	115—205
β—Bi_2Pt	12.9	—	90	85—105
BiPt	15.5	15.75	190	170—220

only the bismuth of the eutectic but also the bismuth in the compound will be dissolved. In etching the alloy a portion of the bismuth in the compound goes into solution. Such enrichment in platinum during the separation of Bi_2Pt crystals from the alloy has already been observed by Roessler.[15] Further increase in the concentration of the acid makes it possible to dissolve nearly all of the bismuth in the compound, leaving a residue of finely-divided platinum. Powder X-ray patterns obtained from this residue show extremely diffuse platinum lines. It is probably practicable, by such selective dissolving, to obtain a skeletal platinum catalyst similar to that described for copper and nickel in the dissertation of Kefeli.[16]

The tabular β-Bi_2Pt crystals separated from the alloy were not wholly suitable for X-ray structural investigations. From the Laue diagrams obtained with the X-ray beam directed perpendicular to the plane of the platelet it was established that the crystals have a hexagonal lattice.

2. ALLOYS OF BISMUTH WITH RUTHENIUM, OSMIUM AND IRIDIUM

Alloys of bismuth with ruthenium, osmium and iridium containing 80 – 90% by weight bismuth were prepared in quartz capsules under an argon atmosphere. Metallographic analysis of these alloys showed two-phase structures in all cases. Powder X-ray patterns were obtained for all of the alloys using copper radiation in a chamber 86 mm in diameter. The X-ray patterns showed lines of bismuth and of ruthenium, osmium or iridium, according to the alloy. In none of the X-ray patterns was any appreciable shifting of the back-reflected lines for one phase or the other observed.

The alloys were subjected to etching in nitric acid. There remained as a residue a grey powder in the case of the alloys of bismuth with ruthenium and iridium, and a dark blue powder in the case of the alloys of bismuth with osmium. From all of these powders X-ray patterns were obtained which showed that the etched powders consisted of ruthenium, iridium and osmium, respectively. Thus, bismuth does not form compounds with ruthenium, osmium or iridium by direct alloying.

CONCLUSION

Investigation of the alloys of bismuth with platinum has made it possible to construct a fusion diagram for the bismuth–platinum system. Two compounds are crystallized in the bismuth–platinum system: Bi_2Pt and BiPt. The compound Bi_2Pt melts with decomposition at a temperature ~ 660° C and can exist in the two modifications α and β-Bi_2Pt, with the temperature of the polymorphic transition ~ 390° C. The compound BiPt corresponds to a maximum in the fusion diagram, melts at ~ 760° C, and forms a eutectic mixture with platinum.

The existence of the high-temperature modification β-Bi_2Pt explains the behavior of alloys of the composition of Bi_2Pt at low temperatures. The appearance of superconductivity in a rapidly-cooled alloy is due to the presence in the alloy of crystals of the superconducting high-temperature modification. The data obtained for the bismuth–platinum system do not as yet permit determination of the reason for the great diversity in T_c for the compound BiPt.

Investigation of the alloys of bismuth with ruthenium, osmium and iridium has shown that ruthenium, osmium and iridium do not form compounds when directly alloyed with bismuth. The data obtained for bismuth–iridium alloys provide confirmation of a previous investigation.[17]

We would like to take this opportunity to express our gratitude to Professor G. S. Zhdanov for his valued counsel and direction in the course of the present work, and to R. N. Kuz'min and A. I. Soklakov for their aid in carrying out the experiments.

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The Penetrating Component of Extensive Cosmic Ray Showers in the Atmosphere

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We have investigated the spatial distribution of μ mesons arising from extensive air showers initiated by primary particles of various energies. It was found that within experimental errors the spatial distribution function for μ mesons did not depend on the energy of the primary particle. The number of μ mesons produced varied with the energy of the primary particle in such a way as to confirm the supposition, advanced previously, that the manner in which energy is distributed among the secondary particles in an elementary nuclear interaction changes at an energy of about 10^{15} ev.

IT HAS BEEN ESTABLISHED by many experiments[1] that the penetrating component in extensive air showers consists both of particles which react strongly with various nuclei, and those which do not (μ mesons). There are more of the latter (passive) particles than of the former (active) ones. In the following we describe the results of an investigation carried out in the summer and fall of 1954 at an altitude of 3860 m (Pamir) on the passive part of the penetrating component of showers.

1. EXPERIMENTAL SETUP

To study the spatial distribution of charged particles in extensive atmospheric showers, we investigated individual showers, using a large number of counters in a hodoscopic arrangement. For each shower of interest we found where the axis of the shower was, the spatial distribution of charged particles, and the total number of particles in the shower at the plane of observation. Penetrating par-