EFFECT OF ANTIMONY AND LEAD IMPURITIES ON PHASE TRANSITIONS IN BISMUTH

N. B. BRANDT and N. I. GINZBURG

Moscow State University

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The effect was investigated of impurities of Sb (from 0 to 2.5 wt.%) and Pb (from 0 to 1.2 wt.%) on the phase transitions in Bi under pressure. It was found that with increase of the Sb concentration the region representing the existence of the Bi II modification in the phase diagram became narrower and apparently disappeared completely at Sb concentrations greater than 0.8 wt.%. The Pb impurity did not appreciably affect the nature of the phase diagram. The results are discussed on the basis of data on the change of the energy spectrum of Bi electrons caused by the Sb and Pb impurities.

In connection with investigations of the effect of Sb and Pb impurities on the energy spectrum of electrons in Bi[1,2] it was of particular interest to determine how these impurities affect the nature of the pressure-temperature phase diagram of Bi.

To investigate the phase transitions we used a technique described earlier in detail.[3] Samples of 1.9 mm diameter and about 3 mm length, coated with a thin layer of graphite lubricant, were compressed between two pistons in the cylindrical channel of a steel yoke using a mechanical press fitted with two reduction gear mechanisms, permitting smooth motion of the pistons when a crank was rotated. One rotation of the crank displaced the pistons by 2.5×10^{-3} mm. The elastic deformation of the yoke and the frame of the press on compression of the sample was measured with strain gauges connected in a bridge circuit. These measurements gave the dependence of the change in the potential difference ΔW across the strain gauges on the number of rotations n of the crank, which is proportional to the displacement of the pistons. At a phase transition accompanied by a change of volume of the sample by ΔV, the $\Delta W(n)$ curves have nearly horizontal portions—"plateaus"—the lengths of which are governed by the magnitude of ΔV.

Samples were prepared from Bi of Hilger brand, 99.998% pure, purified by twenty recrystallizations in vacuum; the Sb and Pb samples were also of Hilger brand. In some cases the original material was Bi of Johnson brand and 99.999% purity. The alloys were prepared in ampoules of Pyrex glass and subjected to annealing in the molten state for 2—3 hours at about 400° C, followed by annealing for 20—30 days at temperatures of ≈ 260 and ≈150° C.

Altogether eight Bi—Sb samples (0, 0.4, 0.6, 0.8, 1.0, 1.5, 2.0, 2.5 wt.% Sb) and three Bi—Pb samples (0.036, 0.06, 1.26 wt.% Pb) were investigated. At these concentrations Bi—Sb and Bi—Pb alloys form a continuous series of solid solutions.[4,5]

Figures 1 and 2 show the dependence of ΔW on n for the original Bi and some of the Bi—Sb and Bi—Pb alloys at 20° C. For convenience the curves are displaced with respect to one another along the ordinate axis. The two "plateaus" in the $\Delta W(n)$ curve of Bi represent the phase transitions Bi I ⇄ Bi II and Bi II ⇄ Bi III, which, at ≈300° K, occur at pressures of 25 300 and 27 000 atm, respectively. In the pressure-temperature phase diagram the crystal modifications Bi I and Bi III are separated by a narrow region in which the Bi II modification is stable; the width of this

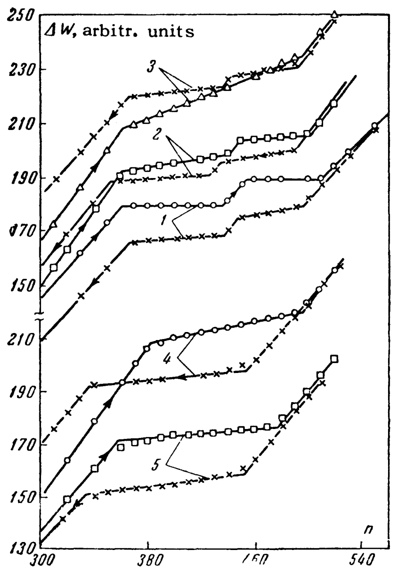

FIG. 1. Phase transitions in the Bi-Sb system at 20° C: 1) pure Bi; 2) 0.4 wt. % Sb; 3) 0.6 wt. % Sb; 4) 0.8 wt. % Sb; 5) 1.5 wt. % Sb.

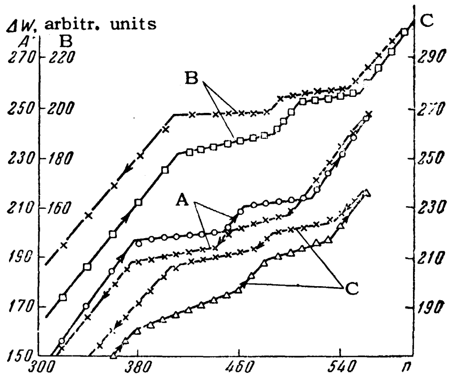

FIG. 2. Phase transitions in the Bi-Pb system at 20° C: A) samples with 0.036 wt. % Pb; B) 0.06 wt. % Pb; C) 1.26 wt. % Pb.

region at room temperature is about 1700 atm. This region narrows on reduction of temperature and apparently disappears completely at about 100° K,[3,6,7] below which the Bi I ⇄ Bi III transition occurs. The sloping portion of the ΔW(n) curve between the two "plateaus" represents this region. On increase of the Sb concentration the width of this sloping portion decreases.

In the Bi—Sb sample containing 0.6 wt.% Sb the Bi I and Bi III modifications are separated by a very narrow region of pressures which appears only in the ΔW(n) curve recorded with the pressure decreasing. In the curve obtained with the pressure increasing the Bi II → Bi III transition is masked by the steep slope of the "plateaus." In the sample containing 0.8 wt.% Sb the two "plateaus" again practically coalesce and in samples having still more Sb(> 0.8 wt.%) only one "plateau" is observed with pressure increasing or decreasing; the length of this plateau, when reduced to the same initial length of the sample, is equal to the sum of the lengths of the two "plateaus" corresponding to the transitions Bi I ⇄ Bi III and Bi II ⇄ Bi III in pure Bi.

Thus, on increase of the Sb concentration, the narrow region separating the Bi I and Bi III modifications in the Bi phase diagram gradually narrows and disappears completely at Sb concentrations greater than 0.8 wt.%. In the latter case increase of pressure produces the Bi I → Bi III phase transition[1)] with a volume change of 7.4%, equal to the sum of the changes (4.5 and 2.9%) during the transitions Bi I ⇄ Bi II and Bi II ⇄ Bi III.[2)] In contrast to Sb, the Pb impurity, as shown by Fig. 2, has practically no influence on the nature of the phase diagram.

From [1,2] it follows that the mechanisms of the influence of Sb and Pb impurities on the energy spectrum of electrons in Bi are different. Pb atoms, having an atomic volume similar to Bi atoms, leave the lattice parameters of Bi practically unaltered at Pb concentrations up to 0.1 wt.%. Pb acts as an "inefficient" acceptor in Bi which reduces the density of conduction electrons. To reduce this density by unity about 75 Pb atoms are needed at the temperature of liquid helium. As the concentration of Pb is increased to 0.06 wt.% the volume enclosed by the electron Fermi surface decreases approximately by 60% but the surface remains similar to the original in shape. The electron density decreases by the same percentage.

Sb and Bi are in the same group in the periodic table. As an impurity Sb, even at low concentrations (up to 2—3 wt.%), reduces considerably the lattice parameters of Bi (0.8 wt.% Sb reduces the lattice parameters of Bi by 0.5% along the trigonal axis and by 0.1% at right angles to this axis). The electron density in the conduction band is also reduced by the presence of Sb: the reduction is about 37% for 0.8 wt.% Sb. Earlier[2] it has been shown that the change in the energy spectrum of electrons in Bi at helium temperatures due to an Sb impurity present in low concentrations is mainly due to the changes in the crystal lattice parameters.

Comparing these previous results with those of the present work we can see that the Pb impurity, which produces a greater change of the electron part of the Fermi surface than the Sb impurity, does not appreciably affect the nature of the phase transitions and the phase diagram of Bi. Conversely, the Sb impurity, which produces smaller changes in the electron part of the Fermi surface than does Pb, produces qualitative changes in the phase diagram of Bi. Thus the nature of the pressure-temperature phase diagram of Bi is not directly related to changes in the volume enclosed by the electron part of the Fermi surface, occurring at helium temperatures, but is very sensitive to changes in the crystal lattice parameters. On the other hand, the fact that the nature of the phase diagram is not altered by Pb present in a concentration of 1.26 wt.% indicates that the change in the diagram caused by 0.7 wt.% Sb (1.2 at.% Sb) is not simply an impurity concentration effect due to the presence of foreign atoms in the Bi lattice.

Concluding, we thank A. I. Shal'nikov for his interest in our work.

[1)]The direct transition from Bi I to Bi III is also confirmed by experiments on the superconducting properties of the Bi III modification with Sb as an impurity.

[2)]This result is in qualitative agreement with the work of Bridgman,[8] who investigated the effect of pressure on the electrical resistance of polycrystalline wires of Bi-Sb alloys.

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