Pressure-induced superconductivity in Bi$_{0.85}$Sb$_{0.15}$ alloy

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Abstract. Pressure variation of the electrical and structural properties of bismuth-antimony alloy at the composition of $x = 0.15$ (Bi$_{0.85}$Sb$_{0.15}$) has been studied by electrical resistivity and synchrotron radiation x-ray diffraction measurements up to 10 GPa. The crystal structure changes from the A7 structure to the incommensurate host-guest composite one at 3 GPa and room temperature. Temperature dependence of the resistivity greatly changes from the semiconducting behaviour to the metallic one associated with the structural phase transition. Pressure-induced superconducting transition of Bi$_{0.85}$Sb$_{0.15}$ is observed above 4.5 GPa. The transition temperature $T_c$ is found to decrease from 6.79 GPa at 4.5 GPa to 5.82 K at 9.5 GPa with increasing pressure.

1. Introduction
We have studied the effect of pressure on the superconductivity and the structural property in bismuth alloys [1-3]. Bismuth forms a substitutional solid solution with antimony (Bi$_{1-x}$Sb$_x$) over the full range of relative concentrations. Bi$_{1-x}$Sb$_x$ crystallizes in the A7 structure (Fig. 1(a)) with space group R-3m at ambient condition. When Bi$_{1-x}$Sb$_x$ at the compositions $x \geq 0.035$ is pressurized, the A7 structure directly changes to the incommensurate host-guest composite one (hereafter “the composite structure”, Fig. 1(b)) with superspace group $I'4/mcm(00\gamma)0000$, where $I'$ denotes the centering $(1/2, 1/2, 1/2, 1/2)$ in superspace, without an intermediate phase corresponding to phase II in pure Bi [4-7].

The composite structure is the same as those for phase III of Bi (Bi-III) and phase II of Sb (Sb-II) [6, 7], which are the high-pressure phases in the pure elements. In both phases, pressure-induced superconducting transitions are observed: the transition temperatures $T_c$ are 6.8 K at 2.9 GPa for Bi-III [8] and 3.7 K at 9.5 GPa for Sb-II [9], respectively. From these experimental results in the pure elements, pressure-induced superconducting transition is also expected to be observed in their solid solution alloy Bi$_{1-x}$Sb$_x$. Indeed, Il’ina reported the superconductivity of Bi$_{1-x}$Sb$_x$ under high pressure in the composition range $x \leq 0.2$ and $0.7 \leq x$ in 1976 and 1980 [10, 11].

Additionally, the band structure of Bi$_{1-x}$Sb$_x$ continuously changes with Sb concentration; it has been well known as semimetal ($x \leq 0.07$, $0.22 \leq x$) and semiconductor ($0.07 < x < 0.22$) so far [12]. Recently, Hsieh et al. reported that Bi$_{1-x}$Sb$_x$ alloys at the composition $0.07 < x < 0.22$ represents a strongly spin-orbit-coupled insulator (a topological Dirac insulator) [13]. Since then, it has attracted...
much attention in basic and applied research. We have performed the electrical resistivity and synchrotron radiation x-ray diffraction measurements of Bi$_{1-x}$Sb$_x$ to investigate pressure-induced superconductivity and study how the high-pressure behaviour of Bi$_{1-x}$Sb$_x$ varies with Sb concentration. Consequently, we observed the superconducting transitions with zero resistance; $T_c$ are $\sim 6.7$ – $7.1$ K at around 3–4 GPa for $x = 0.15$, 0.4, 0.6 and 4.6 K at 8 GPa for $x = 0.8$. The effect of pressure on the superconductivity changes from negative for $x \leq 0.6$ to positive for $x = 0.8$. In this paper, we report the experimental results obtained at the composition $x = 0.15$ (Bi$_{0.85}$Sb$_{0.15}$).

Figure 1. Schematic of crystal structures of Bi$_{1-x}$Sb$_x$: (a) A7 structure, (b) incommensurate host-guest composite structure

2. Experimental
Polycrystalline Bi$_{0.85}$Sb$_{0.15}$ alloy was prepared from grains of Bi and Sb with 99.999% purity purchased from Kojundo Chem. Lab. Co., LTD. The stoichiometric mixture of them with a weight of ~5 g was loaded into quartz tube, which was sealed in a vacuum. It was completely melted at temperature of 420°C for 24 hours, and then quenched in water at ambient temperature. To obtain a homogeneous alloy, a quenched-sample was annealed at temperature of 264°C for 1 week. All peaks in the x-ray diffraction pattern of the product were indexed by the trigonal symmetry with space group R-3m; lattice parameters at 1 atm are $a = 4.5186 \pm 0.0022$ Å and $c = 11.774 \pm 0.008$ Å. The chemical composition was estimated to be roughly $x \sim 0.145$ from lattice parameters since a linear relation exists between the lattice parameters of Bi$_{1-x}$Sb$_x$ and the concentrations of constituent elements.

The electrical resistivity measurement of Bi$_{0.85}$Sb$_{0.15}$ under high pressure was performed using a modified Bridgman anvil cell up to 9.5 GPa [14, 15]. A sample with a size of 1.0 × 0.5 × 0.3 mm$^3$ was cut out of a small fragment flattened under load. It was placed into a Teflon capsule filled with the mixture of Fluorinert (FC-70 : FC-77 = 1:1) as the pressure-transmitting medium for quasi-hydrostatic compression. After compression at room temperature, the cell was cooled to $T \sim 3$ K at each pressure by the Gifford-McMahon 4K cryogenic refrigerator developed by Iwatani industrial gases corporation.

The high-pressure x-ray diffraction measurement was carried out at room temperature using a diamond anvil cell with a culet of 0.6 mm in diameter. The powder sample was placed into a sample chamber, 250 μm in diameter and 99 μm thick, made by drilling a small hole in a SUS301 gasket. For hydrostatic compression, the hole containing the sample was filled with helium fluid compressed to 180 MPa as the pressure-transmitting medium. The diffraction patterns were measured in beamline PF-AR-NE1 of High-Energy Accelerator Research Organization (KEK) in Japan. The incident beam was tuned to 30.19 keV ($\lambda = 0.41066$ Å). Experimental pressure was determined by the ruby fluorescence method.

3. Results and Discussion
Figure 2 shows pressure dependence of the electrical resistivity up to 9.5 GPa at room temperature. The resistivity substantially increases from 2.7 GPa with increasing pressure reaching a maximum at 3.6 GPa, and then shows a sharp drop up to 4.5 GPa. Beyond 4.5 GPa, the resistivity monotonically decreases with pressure. We show in inset of Fig. 2 the electrical resistivity plotted as a function of temperature on compression. Temperature dependence of the resistivity for Bi$_{0.85}$Sb$_{0.15}$ obviously changes between 2.0 and 4.5 GPa where a significant variation in resistivity by pressure is observed; the semiconducting behaviour on cooling to $T \sim 100$ K below 2.0 GPa and the metallic one above 4.5 GPa. These results suggest that the phase transition occurs at pressures of 3 to 4 GPa.

Pressure-induced superconductivity in Bi$_{0.85}$Sb$_{0.15}$ appears above 4.5 GPa. The electrical resistivity sharply drops to zero as shown in inset of Fig. 3. We estimated the value of $T_c$ at the onset temperature
of the transition (intersection of broken lines in inset of Fig. 3): $T_c$ for Bi$_{0.85}$Sb$_{0.15}$ is 6.79 K at 4.5 GPa. It is nearly equal to the value of $T_c$ at 2.9 GPa for Bi-III. The variation of $T_c$ with pressure is shown in Fig. 3. The value of $T_c$ decreases from 6.79 K at 4.5 GPa to 5.82 K at 9.5 GPa with increasing pressure. The transition width, which is the difference between the onset temperature of the transition and the zero resistance critical temperature, is less than 0.2 K at all pressures.

Figure 4 shows the x-ray diffraction patterns at pressures of 0.19 to 10 GPa. All of reflections observed below 2.3 GPa were indexed by the trigonal symmetry with space group $R\bar{3}m$, the A7 structure. On further compression, the diffraction pattern changes at 3.0 GPa, indicating the structural phase transition. The profile obtained at 3.0 GPa is explained by the composite structure reported by Häussermann et al. [4]. Additionally, their report shows that the transition pressure from the A7 structure to the composite one varies linearly with Sb concentration and is estimated to be ~3 GPa for Bi$_{0.85}$Sb$_{0.15}$. Hence, our result agrees well with the estimation.

Comparison of the structural and transport properties show that the variation in resistivity at pressures of 3 to 4 GPa is attributed to the structural change to the composite structure and the composite structure is metallic. The monotonic change in temperature dependence of resistivity above 4.5 GPa, shown in the inset of Fig. 2, indicates that there is no structural change induced by temperature. Therefore, the superconducting phase of the Bi$_{0.85}$Sb$_{0.15}$ alloy has the composite...
structure. The negative effect of pressure on $T_c$ for Bi$_{0.85}$Sb$_{0.15}$ is consistent with those for Bi-III and Sb-II having the composite structure. Though the superconducting transition in the A7 structure is reported in phase I of Sb (Sb-I), the values of $T_c$ for Sb-I, which are less than 1 K, are much lower than the present results and its pressure effect is positive [9].

Previous work on Bi$_{1-x}$Sb$_x$ by Il’ina has shown the superconducting properties at the compositions of $x = 0.03, 0.05, 0.08, 0.12,$ and $0.20$ [10]. The results for $x = 0.12$ in Ref. 10 are plotted in Fig. 3 together with our results. While $T_c$ decreases at pressures above 4 GPa in both results, the significant difference is an increase in $T_c$ for $x = 0.12$ in the pressure range of 3–4 GPa. From the structural study of Bi$_{1-x}$Sb$_x$ [4], it is estimated in $x = 0.12$ that the structural phase transition takes place at ~3 GPa as in the case of $x = 0.15$. Taking the magnitude of the error in the value of $T_c$ into consideration, the increase in $T_c$ for $x = 0.12$ may be associated with a gradual increase in the volume fraction of the superconducting phase, which is the composite structure, accompanied by the phase transition. The reason why this increase in $T_c$ is not observed in our result is probably that the phase transition occurs sharply by compression under good hydrostatic condition at room temperature.

In summary, we performed the electrical resistivity and x-ray diffraction measurements of Bi$_{0.85}$Sb$_{0.15}$ under high pressure up to 10 GPa. A structural phase transition is observed to occur at 3 GPa and room temperature from the A7 structure to the incommensurate host-guest composite one accompanied by a significant change in the electrical resistivity. Pressure-induced superconductivity appears above 4.5 GPa. The transition temperature $T_c$ for Bi$_{0.85}$Sb$_{0.15}$ is 6.79 K at 4.5 GPa and decreases to 5.82 K at 9.5 GPa with increasing pressure. By comparison of the structural and electronic properties, we conclude that the superconductivity of Bi$_{0.85}$Sb$_{0.15}$ is attributed to the incommensurate host-guest composite structure.

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