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Temperature dependence of electrical conductivity and thermoelectric power of Bi-Sb tapes prepared by liquid quenching

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Abstract. Electrical conductivity and thermoelectric power of liquid-quenched Bi-Sb tapes with Sb concentration in the range 8 to 18 at.% are reported between 77 K and room temperature. Analysis of the data shows that the total electrical conductivity of these tapes is determined by a temperature-independent component due to band conduction, and a strongly temperature-dependent part due to carrier transport across or through the defect states. These defect states which appear to originate from structural imperfections and disorders due to rapid cooling, are formed close to the mobility edge within a small energy range.

Keywords. Bismuth-antimony alloy; liquid quenching; thermoelectric power; electrical conductivity; localized states; thermally activated tunnelling.

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1. Introduction

Semimetallic to semiconducting transition in Bi-Sb alloys takes place in the vicinity of 4 at.% of Sb in Bi, because the overlap energy between the L-point electron band and the T-point hole band becomes zero and beyond 40 at.% Sb in Bi the alloy returns to the semimetallic state. Between 4 and 40 at.% of Sb in Bi, the alloy Bi-Sb remains in the semiconducting state. The physical properties of bulk Bi-Sb alloys, as well as their thin films have been widely investigated (Jain 1959; Tanuma 1961; Horst *et al* 1968; Thomas and Goldsmid 1968; Lemmer *et al* 1968; Inoue *et al* 1974). From the study of the temperature dependence of d.c. resistivity and the frequency dependence of a.c. conductivity on vacuum-deposited Bi and Bi-Sb thin films, several workers (Garcia *et al* 1972; Inoue *et al* 1974, 1979; Takabe *et al* 1986) have reported the presence of amorphocity. The formation of localized states at the edge of L-point energy band, T-point valence band and the acceptor levels above T-point hole band have been suggested to explain their results. Such localized states originate from a large number of lattice defects present in the films (Takabe *et al* 1986).

The lattice defects can also be produced by liquid quenching. The nature of electronic states due to defects can be ascertained from the study of electrical transport properties. The present communication reports our results on the temperature dependence of electrical conductivity and the thermoelectric power of liquid quenched $Bi_{1-x}Sb_x$ tapes prepared by the melt spinning technique.

2. Experimental

Bi-Sb alloy ingots (with 8·28, 9·87 and 18·96 at.% Sb) were prepared from 99·999% pure Bi and Sb following the usual method. Ductile tapes (25–30 μ thick) were obtained by ejecting molten Bi-Sb alloy through a narrow nozzle under argon gas pressure on a 30 cm dia copper disc spinning at 2500 revolutions per minute. However, it was observed that good quality tapes of Bi-Sb with Sb concentration > 25 at.% are very difficult to prepare by melt spinning due to the extreme brittle nature of the tapes. X-ray diffraction of Bi-Sb alloy ingot was taken using MoK_α ($\lambda = 0{\cdot}71$ A) radiation. The X-ray pattern of the quenched tapes shows a change in the intensity of X-ray lines. The (102) line still remains the strongest, while the other lines are reduced considerably. This shows that the quenched Bi-Sb tapes are polycrystalline with preferred orientation along the (102) plane.

Electrical resistivity and thermoelectric power of these tapes were measured in a conventional cryostat between 77 and 300 K, using four-probe and differential methods respectively. Calibrated copper-constantan thermocouples were used for temperature measurement. All voltages were recorded with a resolution of 1 μV using a digital multimeter (Keithley 191) and the current sources (Keithley 225) were employed to obtain the sample and the heater current.

3. Results

Electrical resistivity (ρ) and thermoelectric power (α) of the above three tapes measured between 77 and 300 K are shown in figures 1 and 2 respectively. Temperature dependence of their electrical resistivities is very close to that reported for Bi-Sb thin

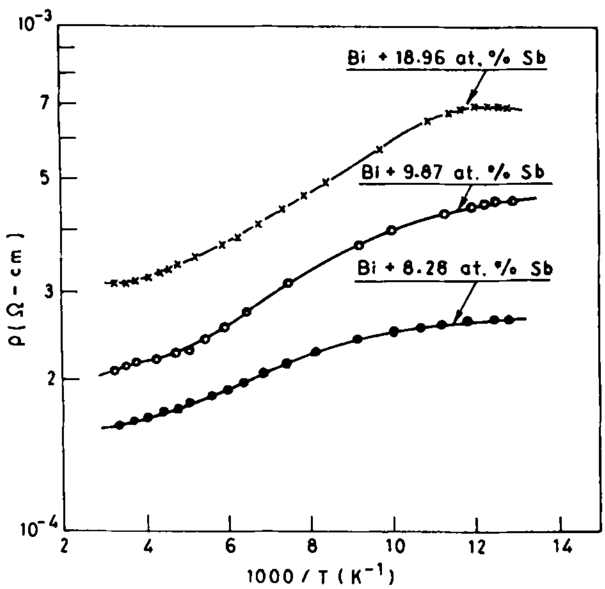

Figure 1. Temperature dependence of the total electrical resistivity of splat-quenched Bi-Sb tapes with different Sb concentrations.

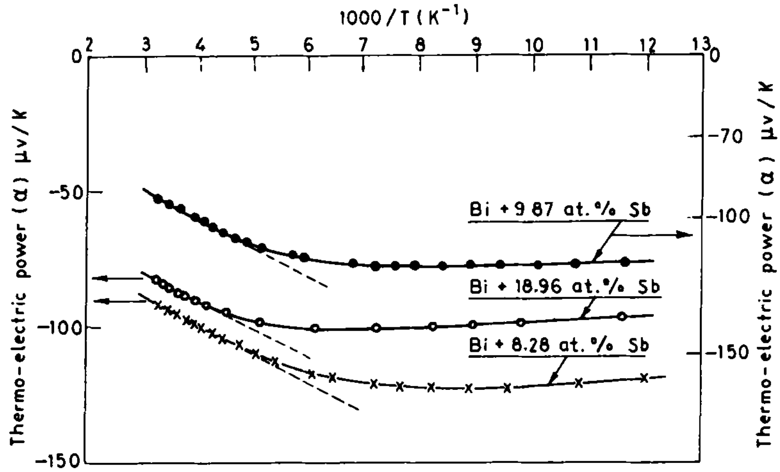

Figure 2. Temperature dependence of thermoelectric power of splat-quenched Bi-Sb tapes with different Sb concentrations.

films prepared by coevaporation (Inoue *et al* 1979) and also by ion beam mixing (Ibrahim and Thompson 1985). Resistivity increases with lowering of temperatures and finally reaches a residual constant value. The magnitude of this residual value (ρ_0) increases with Sb content in Bi. The thermoelectric power of these tapes is negative and their magnitudes are similar to that reported for Bi-Sb bulk alloys (Tanuma 1961) and thin films (Ibrahim and Thompson 1985). At higher temperatures, the thermoelectric power of these tapes varies linearly, while a weak temperature dependence is exhibited at lower temperatures.

4. Discussion

The nature of the temperature dependence observed for the electrical resistivities of the tapes suggests the existence of both temperature-dependent (ρ_h) and temperature-independent (ρ_0) component. Following Inoue *et al* (1979), the total resistivity (ρ) of the tape can be expressed as:

$$1/\rho = 1/\rho_0 + 1/\rho_h \quad \text{i.e.} \quad \sigma = \sigma_0 + \sigma_h$$

where σ's are the corresponding conductivities.

The nature and origin of the temperature-independent part of the conductivity (σ_0) in these tapes may be traced from the semimetallic character of host Bi and from disorders in the samples due to rapid quenching. It is well known that the semimetallic state of Bi goes to the semiconducting state smoothly upon alloying with Sb. The concentration of Sb in Bi, where the band gap opens up lies around 5 at.%. However, the opening of the band gap is also found to be delayed when lattice deformations are present (Goldsmid 1970). As the process of splat cooling produces large imperfections, we might expect an appreciable amount of lattice deformations in our tapes hindering the opening of the band gap. Thus, the Fermi level may still be located in the conduction band giving rise to band conduction (σ_0). Observed decrease of σ_0 with Sb content in host Bi is due to the decrease of the density of states at the Fermi level.

The disorders associated with deformations also create localized states with very small mobility. Electrical conduction can then take place within the localized states, or between the localized and extended states. Such processes are strongly temperature-dependent and give rise to temperature-dependent component of conductivity (σ_h). Under such a situation, several mechanisms (Davis and Mott 1970; Emin 1974) could be responsible for the observed temperature dependence of σ_h. In order to ascertain the possible mechanism, we plotted $\ln \sigma_h$ vs T^{-1} and $\ln \sigma_h$ vs $T^{-1/4}$. While the $T^{-1/4}$ plots do not follow a straight line, the T^{-1} plots yield a linear plot with two different slopes above and below 190 K (figure 3). The thermoelectric power of these tapes is nearly temperature-independent below ~190 K and it varies linearly at higher temperatures (figure 2). The linearity displayed in figure 3 rules out the possibility of either a variable range hopping or small polaron conduction (Emin 1974) in our samples. Further, the existence of two different slopes above and below 190 K (figure 3) along with the temperature variation of thermoelectric power indicates clearly that two different scattering mechanisms are responsible for the temperature dependence of σ_h.

From the above results it appears that below 190 K thermally-activated tunnelling of the carriers across the localized defects states (Davis and Mott 1970) determines the σ_h component of the observed total conductivity of the tapes. This conclusion is also supported by the weak temperature dependence exhibited for thermoelectric power in the same temperature range. Such a temperature-independent thermoelectric power

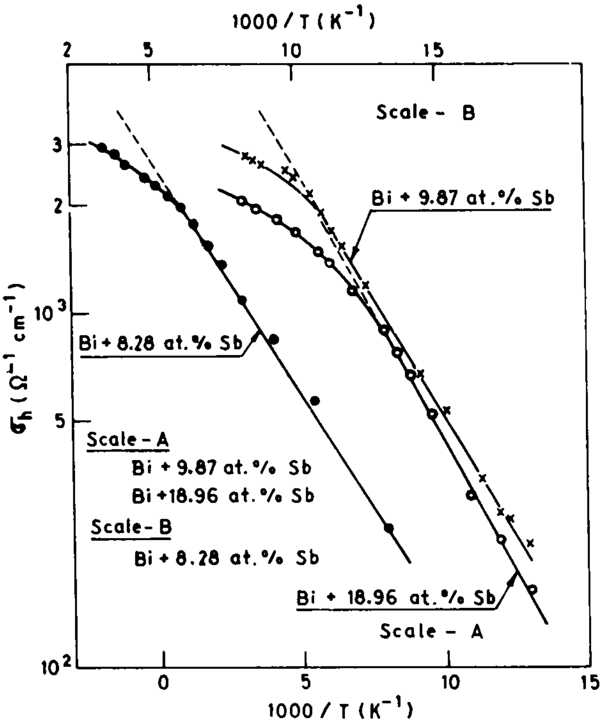

Figure 3. $\ln \sigma_h$ versus T^{-1} for splat-quenched Bi-Sb tapes with different Sb concentrations.

can exist due to ambipolar contribution when conduction is due to thermally activated processes (Fritzsche 1974). Similarly, the exponential dependence of σ_h on T^{-1}, along with the linear dependence of thermoelectric power between 190 K and 300 K, suggests that in this temperature range the conductivity (σ_h) is due to carriers excited beyond the mobility edge (Davis and Mott 1970). Activation energies calculated from ln σ_h vs T^{-1} plot in this temperature range comes out between 9 and 14 meV. These values are much smaller than that of typical disordered semiconductors. This may be due to the narrow band gaps of Bi-Sb compared to the conventional semiconductors.

It may be pointed out that ln σ_h has a smaller slope in the regions where carriers are excited in the extended states beyond the mobility edge, than in the region dominated by thermally activated processes. Though such a feature was reported by Peron (1971) for liquid Se-Te alloys, it is generally not observed for disordered semiconductors. Due to the inelastic nature of thermally activated processes, the larger slopes at low temperatures may be interpreted as due to the smaller spread in energy of the localized states compared to the maximum phonon energy available.

5. Conclusion

Results on the temperature dependence of electrical resistivity and thermoelectric power of Bi-Sb quenched tapes between 77 K and 300 K indicate the presence of localized states. Along with the temperature-independent band conduction (σ_0), a strongly temperature-dependent conductivity (σ_h) contributes to the total electrical conductivity (σ) of the tapes. Below 190 K the component (σ_h) is governed by thermally-assisted tunnelling of electrons between the localized states near the mobility edge; while at higher temperatures it is dominated by electrons excited beyond the mobility shoulders in the extended states. Failure of $T^{-1/4}$ dependence of σ_h suggests that in our quenched tapes there exist very few localized states around the Fermi level. These states are formed mostly close to the mobility edge within a very small energy range.

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