JOURNAL OF MATERIALS SCIENCE 30 (1995) 4339–4342

Electrical properties of semimetallic and semiconducting alloys of Bi–Sb

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Electrical resistivity studies have been carried out on three different Bi–Sb alloys in the temperature range 100–300 K. The observed behaviour of all the samples, in which one is semimetallic and other two are semiconductors, can be explained on the basis of the model presented for Bi–Sb energy bands at low temperature.

1. Introduction

The electronic properties of the group V semimetals, bismuth, antimony and arsenic, are of particular interest because these exhibit small energy gaps, ΔE, in the vicinity of the Fermi energy. These small energy gaps dominate the electronic properties and are responsible for the important similarities between the group V semimetals and the narrow gap semiconductors. All of the group V semimetals crystallize into a lattice with rhombohedral symmetry of the A_7 classification [1], with two atoms per unit cell and five valence electrons per atom. The group V semimetals have a sufficient number of valence electrons to fill completely five bonds. According to crystal binding considerations, it follows that the important electron states are bonding and antibonding S and P states [2]. Of these eight states the bonding S states lie lowest, followed by the antibonding S state, which in turn is followed by the bonding P states and then by the antibonding P states. Calculations of the electron states in the crystal [2, 3] show that the A_7 crystal structure favours the formation of either a semiconductor with five occupied bands separated from the unoccupied bands by a narrow energy gap or a semimetal where some of the electrons in the highest valence states have spilled over into the lowest conduction states, giving rise to a small band overlapping with an equal number of electrons and holes. The states derived from the antibonding P states tend to be empty. In these semimetals, both the bands overlap and certain direct band gaps are small compared with characteristic band widths. In practice, both semiconducting and semimetal are found in the group V materials, the semimetal's behaviour being the more common, though semiconductors can be formed by alloying one semimetal with another, as for example bismuth with antimony. It is interesting to observe that the basic explanation of the semimetal and semiconducting behaviour of these alloys on the basis of a nearly free electron picture was given by Jones as early as 1934 [4, 5]. The various band calculations [2, 3, 6–10] agree that the dominant effect of the rhombohedral shear, which makes the L and T point nonequivalent, is to lower the bands at the L point and to raise them at T. Hence, the band calculations favour the formation of electron pockets around the L point and hole pockets around the T points. There has been controversy with regard to the locations of electrons and holes in bismuth [11–13]. This question was mostly settled by Jain and Koenig [14] who showed the number of electron ellipsoids to be three [15] and of holes to be unity with this counting of the number electron and hole ellipsoids, symmetry arguments indicate the electrons are located either at L or at X and the holes at T or Γ. The energy band model for bismuth [15] strongly favours the location of electrons at L rather than X. Direct experimental support has been given for the T point location of the holes [15].

The carrier density of the group V semimetals is well correlated with the magnitude of the rhombohedral distortion; the longer the distortion, the larger the carrier density. This trend is also consistent with correlation between the rhombohedral distortion and the magnitude of the band separation. At the T and L points in the Brillouin zone: the larger the distortion, the larger the band separations and, hence, the larger the volume of the carrier pockets.

1.1. $Bi_{1-x}Sb_x$ bands

The addition of Sb–Bi results in a decrease in the overlap between the conduction and valence bands resulting in the transition from the semimetallic to semiconducting regime. Heine [16] proposed the transition of bismuth from a semimetal to a semiconductor upon alloying with antimony. A number of investigators [17, 18] have also shown that the L point gap decreases upon adding Sb, with the L point energy levels crossing at some Sb composition. This is reasonable, since Falicov and Lin [17] have shown in Sb that L point conduction and valence bands have the opposite symmetry to those in Bi. Tichovolsky and Mavroides [18] from magnetoreflectance data indicate the L point crossing occurs well before the formation of the semiconducting region ($\langle \sim 4\%$ Sb$\rangle$), while Lerner

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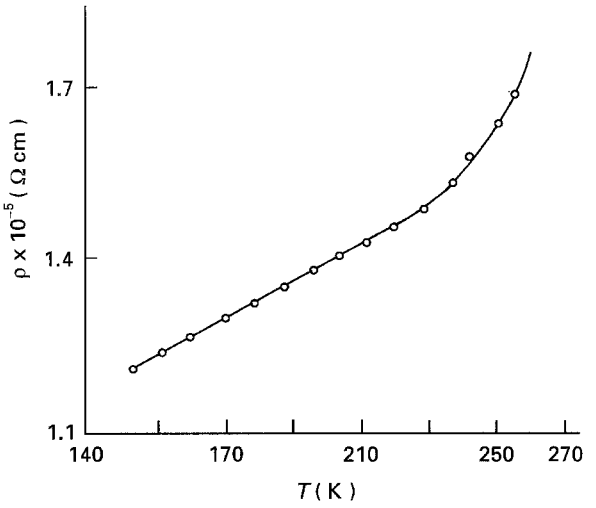

Figure 1 ρ versus T plot in semimetallic Bi–Sb (sample 1).

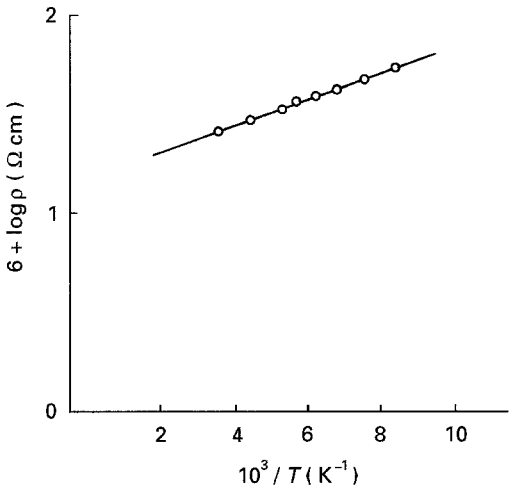

Figure 3 Log ρ versus $10^3/T$ plot in semiconducting Bi–Sb (sample 2) where $\Delta E = 0.002$ eV.

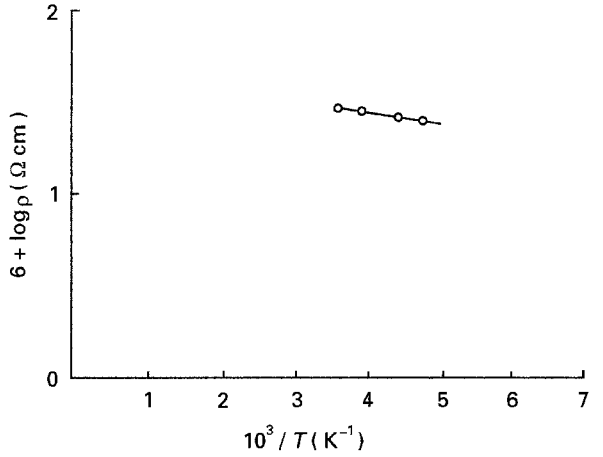

Figure 2 Log ρ versus $10^3/T$ plot in semimetallic Bi–Sb (sample 1) where $\Delta E = 0.003$ eV.

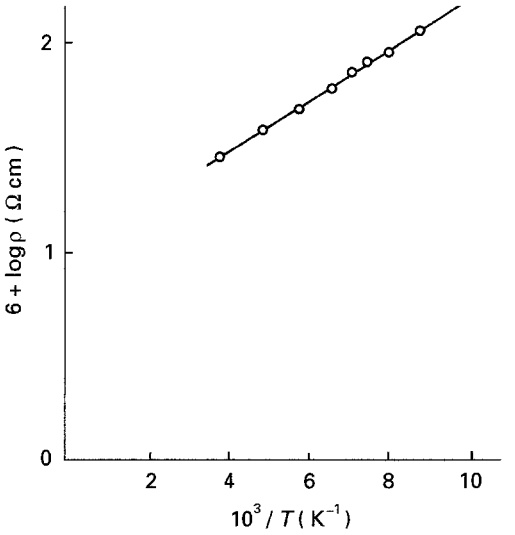

Figure 4 Log ρ versus $10^3/T$ plot in semiconducting Bi–Sb (sample 3) where $\Delta E = 0.004$ eV.

et al. [19] indicate the crossing is quite close to the semimetal semiconductor transition. The investigation of Brandt *et al.* [20] on the motion of the energy band in very high magnetic fields was consistent with the semimetal–semiconductor transition near ~8.5% Sb suggested by Lerner *et al.* Lannin and Cuff [21] suggest a model for Bi–Sb over the range 0–22% Sb. The energy gap at L and the overlap appear to decrease as an approximately linear function of composition up to the order of 10% Sb. Both the semimetal–semiconductor transition and L_s–L_a crossing appear to occur in the region 8–9%, where L_s is the conduction band and L_a is the valence band of Bi [22]. At approximately 22% Sb Wehrli [23] has observed from susceptibility measurements, that the system became semimetallic again. Beyond 22% the bands have not been studied until one reaches pure Sb, where the work of Falicov and Lin [17] indicates that the L_a band contains the electrons in distorted ellipsoid-like surfaces; L_s is directly beneath L_a. Sengupta and Bhattacharya [24] proposed that semimetal–semiconductor transition of Bi–Sb at a temperature range of 100–300 K occurs due to the presence of impurity levels between L_s and L_a bands, but this model does not say anything about why these levels are created and why the semiconductor changes to semimetal when one increases the percentage of Sb to ~25%. An attempt is made in the following section to fit the model of $Bi_{(1-x)}$ Sb_x energy band (which is given for low temperatures) for the experimental data taken in the temperature range 100–300 K.

2. Experimental procedure

Three samples of Bi–Sb alloys were prepared by melting Bi and Sb together in a quartz vacuum tube. The concentration of Sb varies from 5 to 15% by weight. The resistivity measurements were made by the four probe method.

3. Results

3.1. Sample 1, Bi 95–Sb 5 wt%

The resistivity (ρ) versus temperature (T) graph (Fig. 1) shows that at lower temperatures up to ~230 K, the resistivity increases linearly with temperature. Above 230 K resistivity increases exponentially. The plot of log ρ versus $1/T$ gives a straight line (Fig. 2).

3.2. Sample 2, Bi 88–Sb 12 wt%

The variation of electrical resistivity, ρ, versus temperature, T, shows that ρ versus $1/T$ give a straight line (Fig. 3); this shows ρ decreases exponentially with temperature, so this sample is behaving as a semiconductor. The band gap can be calculated by the slope of $\log \rho$ versus $1/T$ curve, and the value of ΔE is 0.002 eV (Fig. 3).

3.3. Sample 3, Bi 85–Sb 15 wt%

This sample is also behaving as a semiconductor. The band gap value from the slope of $\log \rho$ versus $1/T$ is found to be 0.004 eV (Fig. 4).

4. Discussion

4.1. Sample 1

4.1.1. Below ~ 230 K

In this region, the behaviour of the sample is metallic, which indicates that the transport mechanism is metallic in nature; it is probably due to overlap of the L_s (conduction band) and T_{45} (valence band).

4.1.2. Behaviour above ~230 K

In this region $\log \rho$ versus $1/T$ gives a straight line because ρ increases exponentially: there are two possibilities, one is n decreases exponentially, which is not possible because it is highly improbable that the number of free carriers decreases as temperature increases, so the other possibility that the mobility of the hole, μ, decreases exponentially looks reliable.

The gap between L_s and L_a is very small, so as the temperature increases the electrons from L_a move to T_{45} this process decreases the number of holes in T_{45} and increases the number of holes in L_a, as the total number of holes remains constant.

$$P_{L_a} = P \exp - \Delta E/kT$$

$$P_{T_{45}} = P - P_{L_a}$$

where k is the Boltzmann constant, P the number of holes originally present in T_{45} due to overlap of T_{45} and L_s: P_{L_a} and $P_{T_{45}}$ are the number of holes in the L_a band and in the T_{45} band, respectively: ΔE is the energy gap between T_{45} and L_a. Under these conditions the electrical conductivity is

$$\sigma = P_{L_a} \exp \mu_1 + P_{T_{45}} \exp \mu_2$$

where μ_1 and μ_2 are the mobilities of holes in L_a and T_{45} bands, respectively. If the mobility of holes in the T_{45} band is greater than the mobility of holes in the L_s band, then α decreases with temperature

$$\alpha = P_{L_a} \exp \mu_1 + (P - P_{L_a}) \exp \mu_2$$

$$\alpha = P \exp \mu_2 + P_{L_a} \exp(\mu_1 - \mu_2)$$

$$1/\alpha(1 - P \exp \mu_2/\alpha) = 1/P_{L_a} \exp(\mu_1 - \mu_2)$$

$$\rho(1 + P \exp \mu_2/\alpha) = 1/P \exp(\mu_1 - \mu_2) \exp \Delta E/kT$$

$P \exp \mu_2$ and α both decrease slowly with temperature, so one can consider the $P \exp \mu_2/\alpha$ term constant with temperature. So

$$\rho = C \exp \Delta E/kT$$

$$\text{where } C = P/P \exp(\mu_1 - \mu_2)\left(\frac{1 + P \exp \mu_2}{\alpha}\right)$$

The value of ΔE from the slope of $\log \rho$ versus $1/T$ curve (Fig. 2) is 0.003 eV.

4.2. Sample 2 (semiconductors)

It appears as the percentage of Sb increase, the T_{45} band will move down and L_s and L_a come nearer to each other. At around 8–9%, L_s and L_a crossing occurs and T_{45} goes below L_s. So one obtains a semiconductor which has a band gap of ΔE (difference between L_s and L_a). The values of ΔE calculated from the slope of $\log \rho$ versus $1/T$ curve is 0.002 eV.

4.3. Sample 3

Band gap is increased due to further movement of L_s and L_a.

5. Conclusions

The observed properties could be explained on the basis of the model presented for low temperature, that the L_s, L_a and T_{45} bands move as one increases the percentage of Sb. Up to ~9% Sb, the alloy remains semimetallic. After crossover of L_s and L_a takes place and T_{45} goes below L_s, one obtains a semiconductor above ~9%. At approximately ~25% Sb, the alloy becomes semimetallic again. The results also shows that the mobility of holes in T_{45} is larger than in L_a.

Acknowledgements

The authors are grateful to Mr R. S. Nigam for help in preparing the samples.

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Received 19 July 1994
and accepted 22 March 1995