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Electrical properties of undeformed and plastically deformed bismuth–thallium and bismuth–lead systems in the temperature range 4.2 to 300 K

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Measurements of electrical conductivity and Hall coefficient have been made on undeformed and plastically deformed states of Bi–Tl (Bi + 3.92 at% Tl) and Bi–Pb (Bi + 4.00 at% Pb) single-crystal specimens, from 4.2 to 300 K. The carrier concentration n and the Hall mobility μ obtained from these measurements show strong dependence on temperature. From the variation of n with temperature, there is evidence for band gaps of 40 meV obtained from observations between 100 and 300 K for Bi–Tl, and 18 meV between 70 and 300 K for Bi–Pb, in the undeformed states of the specimens. These band gaps increase due to plastic deformation. In the low-temperature region, the increase and the subsequent decrease in n have been explained on the basis of a thermal activation process and a phonon-induced electron–hole recombination process. The activation energies thus observed in the undeformed state of the specimens have been greatly reduced due to plastic deformation. These results show that the band structure of bismuth is greatly affected by doping, and that of the doped specimens of bismuth is further affected by plastic deformation. There is a correspondence between the increase in n and the decrease in μ and vice versa, over the entire range of temperature. The dependence of μ on T has been utilized to identify the scattering mechanisms.

1. Introduction

In recent years, several authors [1–3] have reported measurements on the electrical resistivity of high-purity bismuth specimens at low temperatures. The main consequence of all these investigations appears to be that the electron mean free path exhibits a quadratic dependence on temperature over a fairly wide range. The electrical resistivity of a series of Bi–Sb alloys has been measured by Fenton *et al.* [4]. They found that the addition of antimony preserved the T^2 dependence. Chopra *et al.* [5] measured the electrical resistivity of pure bismuth, Bi–Sb, Bi–Pb and Bi–Te alloys, between 1.3 and 77 K. For all these systems the ideal resistivity shows a T^2 dependence at low temperatures. But the effect of doping bismuth with elements like thallium or lead on the electrical resistivity, when such a system is transformed into a superconductor with appropriate concentrations of either thallium or lead, is likely to be different. The superconducting behaviour of bismuth doped with various concentrations of thallium (between 2 and 9 at % Tl) and lead (between 2 and 7 at % Pb) has been discussed elsewhere [6–8]. The phase diagrams of Bi–Tl and Bi–Pb systems [9, 10] indicate very little solubility of either thallium or lead in bismuth. It is quite likely that thallium or lead atoms exist as impurities in a bismuth lattice. Laue back-reflection photographs [6, 7] of these specimens indicate that the bismuth lattice is gradually distorted with increasing concentration of either thallium or lead. The effect of plastic deformation on the transition temperature T_c and the thermal conductivity has already been reported by us [7, 8]. There is an enhancement of T_c for these systems, 22% in the case of Bi–Pb and 32% in the case of Bi–Tl. Our thermal conductivity measurements [8] show that plastic deformation affects the Debye temperature of the systems. Further, the doping of bismuth with either thallium or lead affects the phonon spectrum, resulting in the change in θ_D. In order to understand the behaviour of the electrical properties of Bi–Tl and Bi–Pb, both in the undeformed and the plastically deformed states, we have measured the electrical conductivity and Hall coefficient of Bi–3.92 at % Tl and Bi–4.00 at % Pb, from T_c to 300 K. The electrical conductivity and Hall coefficient of pure single-crystal specimen of bismuth, between 4.2 and 300 K, have also been measured for comparison.

2. Experimental procedure

The specimens were grown by the Bridgman technique using Johnson Matthey spectrographically standardized materials (99.9999%). The details regarding the growth conditions are discussed elsewhere [6]. The specimens were cut from the grown crystal using the spark erosion technique, and were given a rectangular parallelepiped geometry. The specimens were subjected to a slow lapping process using fine-mesh corborundum powder on a plane glass plate. Each surface was lapped in turn until both the surfaces were parallel to each other. Care was taken to make sure that the rectangular parallelepiped shape was obtained. The specimen dimensions were length 3 cm, breadth 0.3 cm and thickness 0.1 cm. These specimens were used for our measurements after annealing for about 80 h at a constant temperature (about half the melting point of the specimen), to remove strains introduced during cutting and handling.

A three-point technique was used to deform the specimens plastically. The specimen was supported on two quartz knife-edges and heated to a temperature of about 0.5 T_m, T_m being the melting point of the specimen in degree Celsius. It was found by Bell *et al.* [11] that at approximately 0.5 T_m a plastic condition can be attained quite easily. The specimens were bent along a particular orientation by means of a load applied through a third knife-edge at a point between the two supporting knife-edges. The third knife-edge was held vertically by means of spring-loaded platform. On top of the platform were placed suitable weights needed to deform the specimen plastically. When plastic deformation started, there was a depression of the third knife-edge which was indicated by a dial gauge attached to the bottom of the platform. The knife-edges and the heater electrodes were subjected to ultrasonic cleaning in propanol so as not to contaminate the specimen. The deformation was performed in an inert atmosphere to prevent oxidation and impurity contamination of the specimen. A schematic diagram of the set-up has been shown elsewhere [7]. The measurements were carried out in a conventional liquid helium cryostat, using a potentiometric technique. A six-probe technique was used to measure the electrical resistance and Hall voltage. A Rubicon potentiometer with a Leeds and Northrup d.c. null detector (sensitivity 0.01 μV) was used to measure the different voltages. An electronic temperature controller (sensitivity 0.01 K) was used to control the temperature above 4.2 K. The thermometers used were a (gold + 0.07% iron)–chromel thermocouple for temperatures between 4.2 and 77 K and a chromel–constantan thermocouple for temperatures between 77 and 300 K.

Laue back-reflection photographs were taken for these specimens both in the undeformed and deformed states, and transmission-range powder photographs were taken for pure bismuth, Bi–Tl and Bi–Pb. The detailed interpretation of these photographs has been discussed elsewhere [7]. From the photographs it is evident that the single-crystalline nature has not been destroyed by doping, but the symmetry of the bismuth lattice has been disturbed. Deformation tends to make the specimen polycrystalline, but in the case of Bi–Tl the Laue spots are still visible, showing that the single-crystalline nature has not been effectively disturbed. The spots are elongated and diffuse, showing that imperfections have been introduced into the system due to plastic deformation. A powder photograph technique was used to confirm the extent of distortion of the bismuth lattice due to doping with either thallium or lead and to detect any possible structural change brought about by doping. From the transmission-range powder photographs [7] of pure bismuth, Bi–Tl and Bi–Pb it is found that the value of the lattice constant a_0 determined for pure bismuth is 0.4739 nm, which is close to the value reported earlier, a_0 = 0.474 nm [12]. For the Bi–Tl and Bi–Pb systems, a_0 was found to be 0.4786 and 0.4779 nm, respectively. From these values it is quite evident that there has been a distortion of the bismuth lattice due to doping, but there is no definite indication of any structural change due to doping.

3. Results and discussion

3.1. Electrical conductivity of pure bismuth, Bi–Tl and Bi–Pb

Fig. 1 presents the variation of electrical conductivity σ as a function of temperature, in the temperature range 4.2 to 300 K, for a pure bismuth single-crystal specimen. Fig. 1 also gives the variation of σ for the undeformed and plastically deformed states of Bi–Tl and Bi–Pb between T_c and 300 K. The variation of σ with temperature for all the specimens can be divided into three well-defined regions:

(i) The impurity scattering region where σ is constant. For pure bismuth the impurity scattering region does not extend up to 4.2 K, but for Bi–Tl and Bi–Pb in the undeformed state it extends up to 8 and 10 K, respectively.

(ii) The region where σ varies approximately as $T^{-1/2}$. For pure bismuth the region extends from 4.2 to 60 K (here σ varies as $T^{-3/4}$), but for the undeformed states of Bi–Tl and Bi–Pb it extends from 8 to 60 K and 10 to 90 K, respectively.

(iii) The region where σ varies as T^{-1}. For pure bismuth the region extends from 60 to 300 K, but for

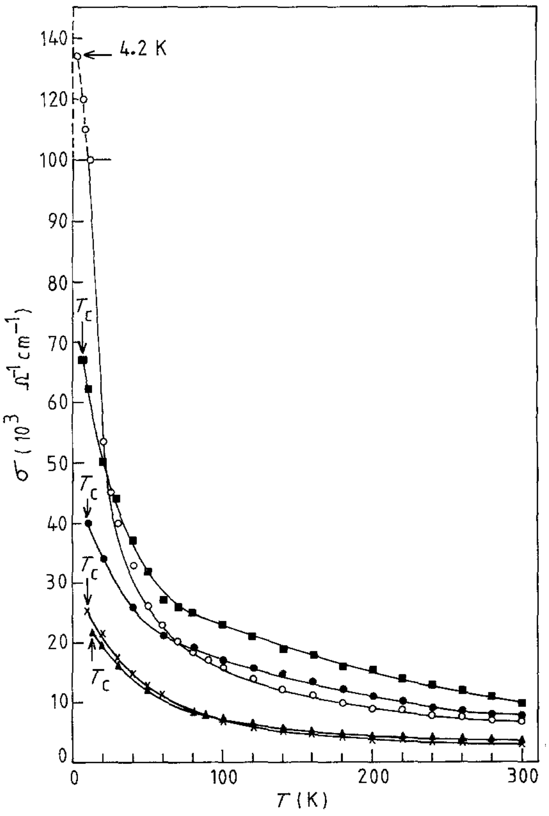

Figure 1 Variation of electrical conductivity σ as a function of temperature: (○) pure bismuth, (■) undeformed Bi–Tl, (●) plastically deformed Bi–Tl, (x) undeformed Bi–Pb, (▲) plastically deformed Bi–Pb.

the undeformed states of Bi–Tl and Bi–Pb it extends from 60 to 300 K and 90 to 300 K, respectively.

Thus, the variation of σ with T in all three cases is more or less similar; only the magnitude of σ is different. Thus, a proper understanding of the variation of σ with T in the case of pure bismuth will help in understanding the allied variations in the other two systems. In the case of bismuth, the decrease of σ with temperature increase in the region 4.2 to 60 K is different from the variations of σ reported by others [1, 3, 4, 13–22] in this temperature range. They have observed a T^{-2} dependence of σ for a limited range of temperature. The electrical resistivity between 4.2 and 300 K can be explained in terms of a simple model which includes residual intervalley and intravalley contributions to the total resistivity [14]. Following Lopez [21], two single-phonon intervalley processes are assumed and reasonable values of the two characteristic phonon energies are found. The approximate T^2 behaviour commonly reported for the electrical resistivity of bismuth emerges as a natural consequence of the above combination of contributions to total resistivity. Between 16 and 77 K the variation of resistivity with temperature is linear. The Bloch–Grüneissen theory of lattice scattering explains the linear dependence of resistivity. Bismuth, because of its very small size of Fermi surface, has a rather low effective Debye temperature, and unlike other metals would be expected to show a linear dependence down to quite low temperatures [22]. However, in order to understand the variation of σ in this range one has to look at the variation of the carrier concentration n and Hall mobility μ. The variation of σ between 60 and 300 K is similar to that reported earlier [14, 22].

3.2. Hall coefficient and carrier concentration

The variation with temperature of the Hall coefficient R_H at 850 G in the temperature range 4.2 to 300 K was utilized to determine the variation of carrier concentration with temperature. For low magnetic fields, the Hall scattering factor is expected to be unity. The carrier concentration n can be estimated from the measured values of R_H according to the relation

$$R_H = 1/ne \qquad (1)$$

where e is the electronic charge. For pure bismuth, n is of the order of $10^{18}\,\text{cm}^{-3}$. The variation of n with T for pure bismuth is shown in Fig. 2. Between 4.2 and 57 K, n increases exponentially with increase in temperature, followed by a region, 57 to 120 K, where n decreases approximately as T^{-2}. It becomes proportional to $1/T$ for temperatures greater than 120 K, up to 300 K.

The increase in n between 4.2 and 57 K may be due to a thermal activation process. A plot of $\ln n$ against $1/T$ in this region gives a straight line. An activation energy of the order of 1 meV has been estimated from the slope of the straight line, in this region. The decrease in n may be associated with a phonon-induced electron–hole recombination process. Similar mechanisms have been discussed by Michenand and Issi [20], Hartman [3] and Lopez [21]. Hartman [3] measured the linear Hall and quadratic magnetoresistance coefficients of bismuth as a function of temperature. The experimental values of carrier density and components of the mobility tensor for electrons and holes as a function of temperature were computed. According to Hartman, because the conductivity varies as T^{-2} the dominant scattering mechanism is not deformation potential scattering, but rather scattering between carriers in separate valleys. The carriers in the different valleys interact via the Coulomb interaction, each remaining in their respective valleys, conserving energy and momentum, though not individually. For carriers of differing charge or of sufficient anisotropy, this mechanism contributes to the resistivity. In support of this mechanism, the electron and hole mobilities at 4.2 K were estimated from the ionized impurity scattering and were in good agreement with the measured mobilities. Lopez [21] measured the electron–hole recombination time in bismuth, at low temperatures. Above 6 K the recombination time decreased rapidly as temperature increased. A model was postulated in which the absorption or emission of a single phonon provides for

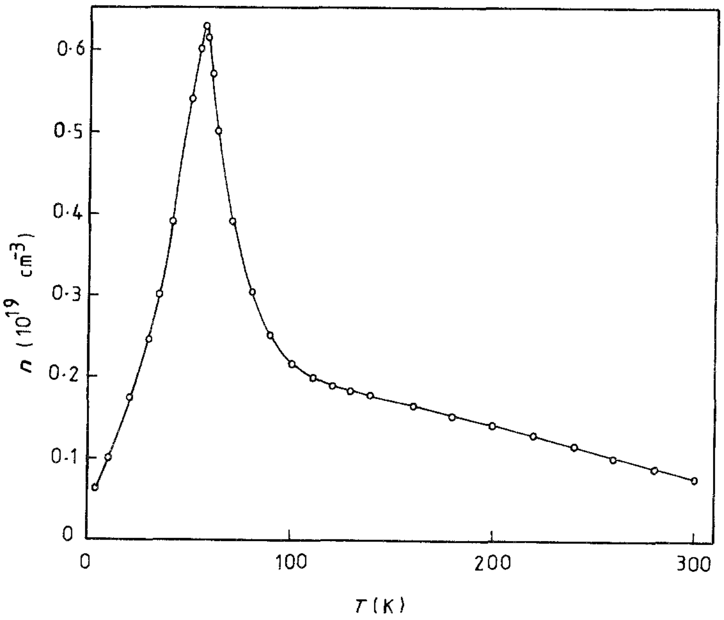

Figure 2 Variation of carrier concentration n as a function of temperature for pure bismuth.

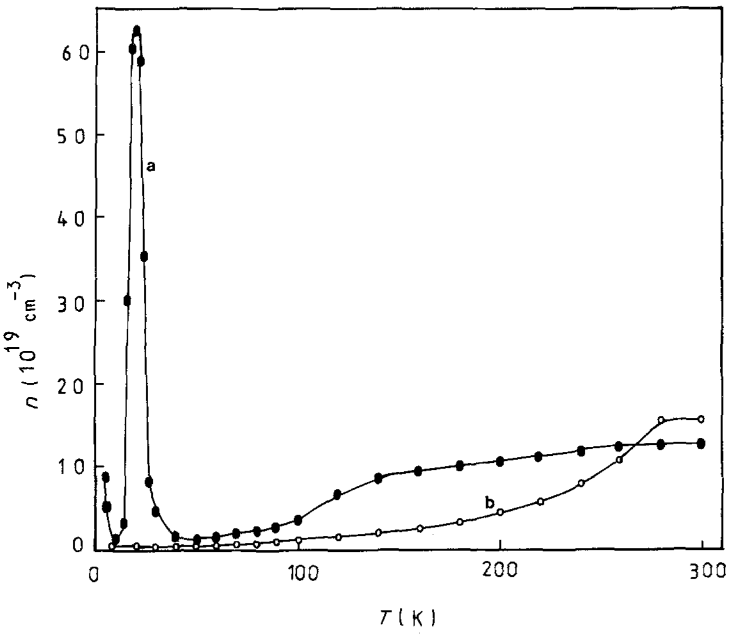

Figure 3 Variation of carrier concentration n as a function of temperature for Bi–3.92 at % Tl: (●) undeformed, (○) plastically deformed.

momentum conservation in the recombination of electrons and holes. Michenand and Issi [20] have also discussed electron and hole transport in bismuth.

Figs 3 and 4 present the variation of n as a function of temperature for the undeformed and plastically deformed states of Bi–Tl and Bi–Pb, respectively, between T_c and 300 K. The carrier concentration n for Bi–Tl and Bi–Pb is of the order of $10^{19}\,\text{cm}^{-3}$. Thus, compared to that of pure bismuth ($n \sim 10^{18}\,\text{cm}^{-3}$) there has been an increase of n due to doping with either thallium or lead. In these systems R_H is found to be negative.

From Fig. 3, for the undeformed state of Bi–Tl, it is found that between T_c and 10 K, n decreases quite sharply with increase in temperature. This is followed by an exponential increase of n up to 20 K. Between 20 and 50 K, n decreases rapidly with increase in temperature. Between 50 and 300 K, n increases with increase in temperature. The variation of n between T_c and 10 K, where n decreases with increase in temperature, is not been properly understood by us. Between 10 and 20 K, n rises exponentially as the temperature increases. A plot of ln n against $1/T$ gives a straight line. The activation energy obtained is of the order of 14 meV. Between 20 and 50 K there is an exponential decrease of n with increase in temperature. In the high-temperature region between 100 and 300 K a plot of ln n against $1/T$ gives a straight line. The band gap computed is of the order of 40 meV. From our thermal conductivity data reported elsewhere [8], in the temperature range 140 to 300 K a band gap of the order of 60 meV has been estimated. In this region the electronic thermal conductivity is found to be dominant, and increases exponentially with temperature. The increase in n between 10 and 20 K may be due to a thermal activation process, and the subsequent decrease in n may be associated with a phonon-induced electron–hole recombination process, as already discussed in bismuth.

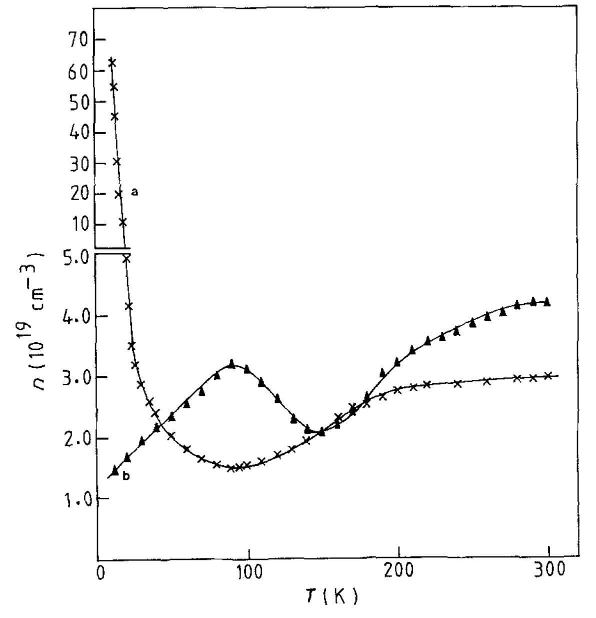

Figure 4 Variation of carrier concentration n as a function of temperature for Bi–4.00 at % Pb: (x) undeformed, (▲) plastically deformed.

From Fig. 4, for the undeformed state of Bi–Pb, it is found that between T_c and 12 K, n is constant. In the region 12 to 30 K, n decreases rapidly with increase in temperature, followed by a gradual decrease of n up to 70 K. The mechanism responsible for this decrease is not clear to us but may be attributed to an electron–hole recombination process as mentioned earlier. In the region 70 to 300 K, n increase with increase in temperature and the linear variation of ln n against $1/T$ is indicative of a band gap of the order of 18 meV.

3.3. Hall mobility

The variation with temperature of the Hall mobility μ for pure bismuth, computed from the relation $\mu = \sigma R_H$ in the range 4.2 to 300 K, is shown in Fig. 5. The mobility μ decreases with increase in temperature between 4.2 and 50 K, and then increases slowly with increase in temperature over the range 50 to 300 K. From Fig. 2 (n against T) we can see that in the region 4.2 to 50 K, where μ decreases with increase in temperature, there is a corresponding increase in n. In the temperature range 50 to 300 K, μ increases with increase in temperature and correspondingly n decreases. Thus, it appears that the variation of μ with

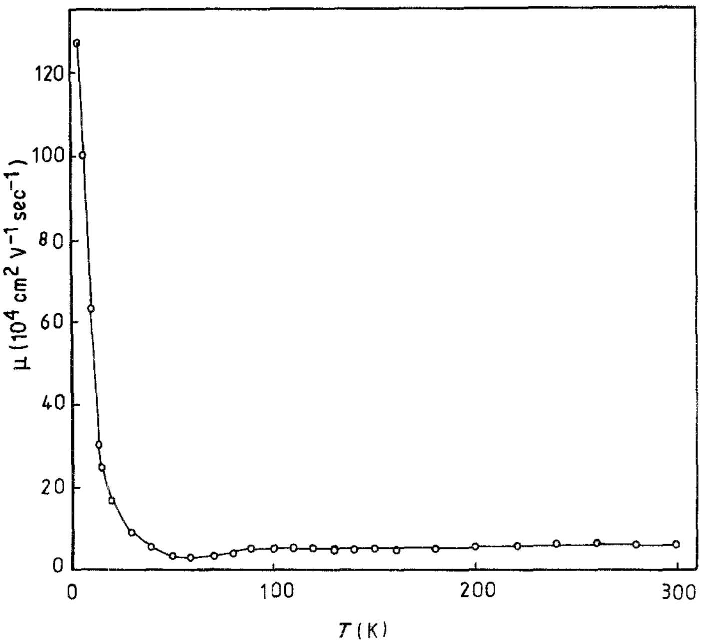

Figure 5 Variation of Hall mobility μ as a function of temperature for pure bismuth.

T is essentially linked with the variation of n with T. We do not have a proper understanding of the variation of n in this temperature range. However, it appears that this variation of n with its dependence on μ is similar to the variations of n and μ due to ionized impurity scattering in the case of semiconductors. It is known from the literature on semiconductor physics [23] that the Brooke–Herring formula for μ due to ionized impurity scattering (IIS) gives

$$\mu_{\mathrm{IIS}} = \frac{2^{7/2}K^2}{\pi^{3/2}m^{*1/2}e^3}\,\frac{(kT)^{3/2}}{N_{\mathrm{I}}}\,\frac{1}{\ln(1+b) - [b/(1+b)]} \tag{2}$$

where $b = (6Km^*/\pi h^2e^2)(kT)^2/n$; N_{I} is the total ionized impurity concentration, K is the static dielectric constant, m^* the effective mass of the charge carrier and n the number of charge carriers per cm^3. Here,

$$N_{\mathrm{I}} = N_{\mathrm{D}}^{+} + N_{\mathrm{A}}^{-} \tag{3}$$

where N_{D}^{+} is the concentration of ionized donors and N_{A}^{-} the concentration of ionized acceptors. The carrier concentration n is expressed as

$$n = N_{\mathrm{D}}^{+} + N_{\mathrm{A}}^{-} \tag{4}$$

From Equations 3 and 4, we see an obvious relation between n and N_{I}:

$$N_{\mathrm{I}} = 2N_{\mathrm{D}}^{+} - n$$

or

$$N_{\mathrm{I}} = n - 2N_{\mathrm{A}}^{-} \tag{5}$$

It is evident from Equation 2 that N_{I} and T are the variable factors in the expression for μ_{IIS}. When all the donors and acceptors are ionized, N_{I} is a constant. Then μ is proportional to $T^{3/2}$. If there are some neutral donors, these will be gradually ionized with increase in temperature and, therefore, the number of ionized carriers will increase and as a result n will also increase. If N_{I} (i.e. n) increases exponentially, as happens in a thermal activation process, then μ will essentially be governed by the increase in n. This means that μ is likely to decrease exponentially. However, because of the $T^{3/2}$ dependence of μ with T, the decrease in μ may be somewhat different. On the other hand, if N_{I} (i.e. n) decreases with temperature, as might happen when carriers are trapped, the mobility will increase. Thus, there is a correspondence between the increase/decrease in N_{I} or n and the decrease/increase of μ. The intervalley electron–electron (e–e) scattering and electron–hole (e–h) scattering reported by many authors [14, 15, 17] for pure bismuth, in which the carriers remain within their valleys before and after collision, may be considered similar to the scattering of carriers by ionized impurities. It would be too much to expect an exact similarity between the ionized impurity scattering due to the presence of ionized donors or acceptors in semiconductors and intervalley e–e or e–h scattering, but there is a similarity of approach. The variation in μ with n can be qualitatively explained from this approach.

The electrical conductivity σ is governed both by the Hall mobility and carrier concentration n and can be expressed as

$$\sigma = ne\mu \tag{6}$$

The observed variation of σ with T is a consequence of the variation of n and μ with temperature.

Figs 6 and 7 present the variation with temperature of the Hall mobility, computed from $\mu = R_{\mathrm{H}}$, for the undeformed and the plastically deformed states of Bi–Tl and Bi–Pb, respectively, over the temperature range T_{c} to 300 K.

From Fig. 6, for the undeformed state of Bi–Tl, we can see that between T_{c} and 10 K, μ increases sharply with increase in temperature. This is followed by a decrease of μ with increase in temperature, up to about 20 K. Between 20 and 50 K there is an increase of μ with increase in temperature. Above 50 K, up to 300 K, there is a decrease in μ as temperature increases. The exact dependence of μ on T is difficult to estimate. The relevant scattering mechanisms in our system may be ionized impurity scattering and deformation potential scattering (DPS). In that case, applying

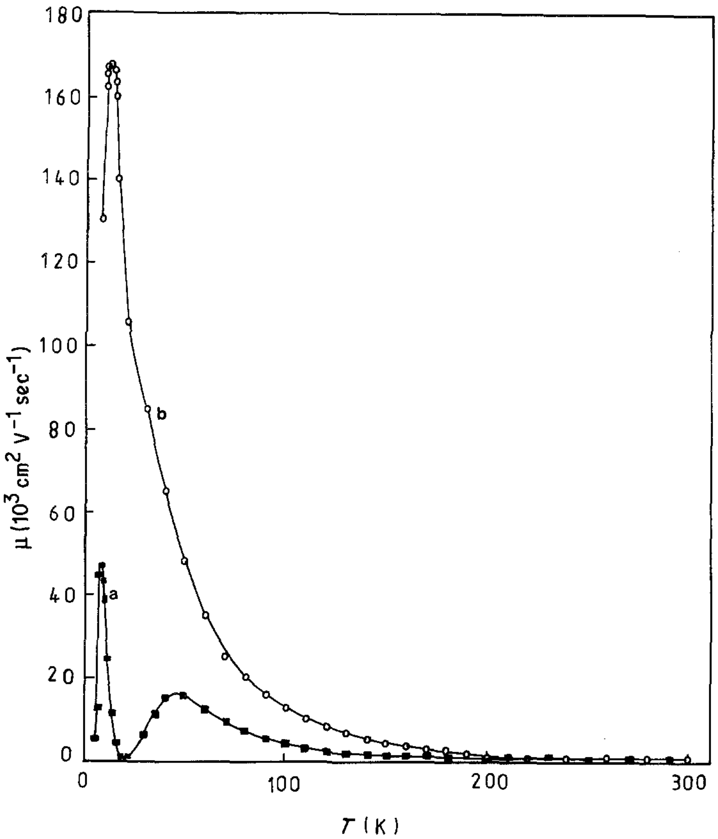

Figure 6 Variation of Hall mobility μ as a function of temperature for Bi–3.92 at % Tl: (■) undeformed, (○) plastically deformed.

Matthiessen's rule, we have

$$\frac{1}{\mu_{\text{eff}}} = \frac{1}{\mu_{\text{DPS}}} + \frac{1}{\mu_{\text{IIS}}} \qquad (7)$$

Since the dependence of μ due to ionized impurity scattering is rather complicated (as mentioned earlier), it is difficult to estimate the relative contributions due to the two mechanisms. It is quite likely that at temperatures greater than 100 K, μ may be essentially determined by deformation potential scattering.

From Figs 3 and 6 we can see that the variation of μ is closely related to the variation of n. As in the case of bismuth, there is a correspondence between the increase/decrease of n and the decrease/increase of μ. There has been a reduction in the μ values over the entire range of temperature in relation to the μ values of pure bismuth. Since μ has been derived from σ, using Equation 6, a proper understanding of the variation of μ with T helps us in assessing the variation of σ with T. The carrier concentration has increased and

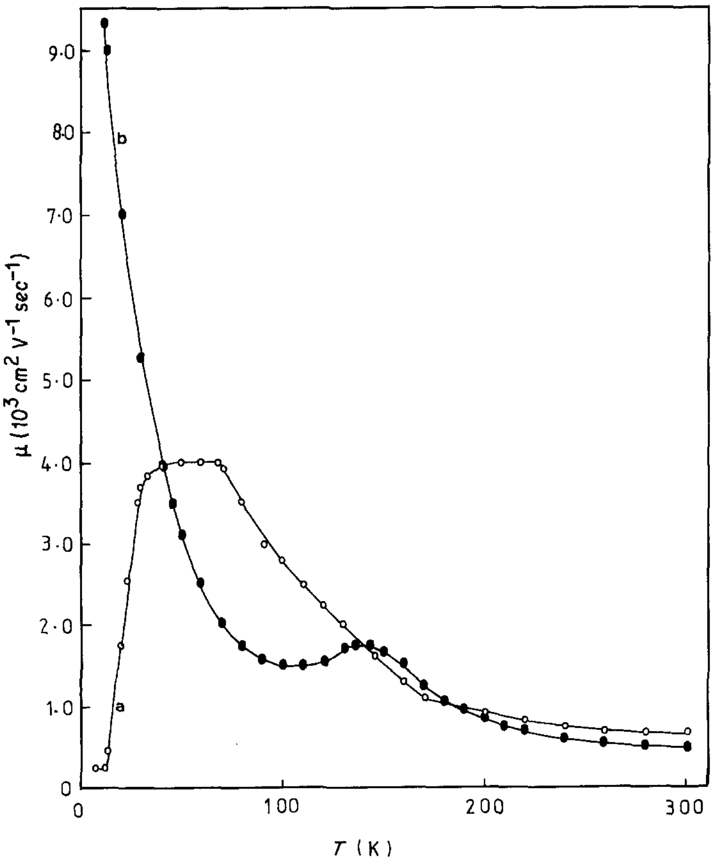

Figure 7 Variation of Hall mobility μ as a function of temperature for Bi–4.00 at % Pb: (○) undeformed, (●) plastically deformed.

the mobility has decreased as compared to that of pure bismuth. The net result is an increase in σ in the region 20 to 300 K.

From Fig. 7, for the undeformed state of Bi–Pb, it is evident that between T_c and 12 K, μ is constant, followed by an increase of μ with increase in temperature up to 30 K. It is almost constant in the region 40 to 70 K. For temperatures greater than 70 K, up to 300 K, μ decreases with increase in temperature. From Figs 4 and 7 we can see that the variations of n and μ are closely related, and this pattern of variation is similar to what has been observed in the case of pure bismuth and the Bi–Tl system.

For the undeformed state of Bi–Tl, approximately from 8 to 60 K, the variation of σ with T follows from the increase and the subsequent exponential decrease of n and a corresponding variation of μ in terms of Equation 2. For higher temperatures, between 100 and 300 K, n increases exponentially. In the same region μ decreases approximately as $T^{-3/2}$ and is essentially governed by deformation potential scattering. The variation of σ with T in this region is consistent with this approach.

For the undeformed state of Bi–Pb in the region 10 to 90 K, the variation of σ with T can be explained on the basis of the exponential decrease of n with temperature increase and a corresponding variation of μ according to Equation 2. For temperatures greater than 100 K, the variations of n and μ are similar to those of Bi–Tl. Thus, the effective scattering mechanism is deformation potential scattering. The observed dependence of σ on T in this region follows from the same reasoning. However, the inverse dependence of σ on T in this region, both for Bi–Tl and Bi–Pb, can be explained on the basis of the Bloch–Grüneissen theory of lattice scattering.

In the Bi–Pb system, μ decreases over the entire range of temperature in relation to the μ values of pure bismuth, but the decrease of μ is greater than that for the Bi–Tl system. This accounts for the decrease of σ for Bi–Pb over the entire range of temperature.

3.4. Effect of plastic deformation on σ, n and μ for Bi–Tl and Bi–Pb systems

3.4.1. Electrical conductivity

The variation of electrical conductivity with temperature in the deformed state of the specimens follows the same pattern as in the case of the undeformed state of the specimens. The impurity scattering region is extended from 8 to 10 K in the case of the Bi–Tl system, and from 10 to 14 K in the case of the Bi–Pb system, due to plastic deformation. This shows the presence of large-scale point imperfections.

For the deformed state of Bi–Tl from T_c to 300 K, Fig. 1 shows that a decrease in σ is observed due to plastic deformation. This decrease is expected in view of the presence of large-scale imperfections in the crystal due to plastic deformation. For the deformed state of Bi–Pb we can see that the behaviour is similar to that of the undeformed state. Plastic deformation has decreased σ for Bi–Pb between T_c and 88 K. Above 88 K, σ is higher for the deformed state, right up to 300 K. The decrease in σ between T_c and 88 K, and the subsequent increase in σ between 88 and 300 K, due to plastic deformation, can be understood from a knowledge of the variation of n and μ in these regions.

3.4.2. Hall coefficient and carrier concentration

For the deformed state of Bi–Tl, Fig. 3 shows that n is effectively constant over the temperature range 12 to 90 K and is followed by a region where n increases exponentially between 100 and 300 K. However, n decreases appreciably from the corresponding value for the undeformed state over the temperature range T_c to 270 K, due to plastic deformation. Between 270 and 300 K, n is higher for the deformed state. The peak observed for n at about 20 K for the undeformed state has completely vanished. This shows that the band structure has been affected. A band gap of the order of 90 meV has been estimated from our observations in the high-temperature region between 100 and 300 K. The band gap has increased due to plastic deformation.

For the deformed state of Bi–Pb, Fig. 4 shows that between T_c and 50 K n increases with temperature and an approximate activation energy of the order of 1 meV has been observed. For temperatures greater than 90 K, up to 150 K, a decrease in n is observed followed by an increase of n with increase in temperature in the region 150 to 300 K. A plot of ln n against $1/T$ gives a straight line in the region 150 to 300 K, showing the existence of a band gap of the order of 50 meV. Plastic deformation has resulted in a decrease of n compared to that of the undeformed state between T_c and 50 K, whereas n for the deformed state is slightly higher than that for the undeformed state in the region 50 to 300 K. Plastic deformation has also enhanced the band gap of the system. Thus, the band structure is affected.

3.4.3. Hall mobility

For the deformed state of Bi–Tl, Fig. 6 shows that between T_c and 11 K the increase of μ with increase in temperature is extremely rapid. Beyond 11 K there is a decrease of μ with increase in temperature, up to 300 K. Plastic deformation has increased the value of μ between T_c and 200 K. Above 200 K, μ values for the deformed state and the undeformed state are identical. Experimental values of μ have been reported by many authors [24, 25]. There is a tendency for crystals with a small energy gap to have high values of mobility. Small gaps lead to a small effective mass which favours high mobility. This aspect is also evident in our case, where μ is of the order of $10^3\,\mathrm{cm^2\,V^{-1}\,sec^{-1}}$ near T_c.

For the deformed state of Bi–Pb, Fig. 7 shows that between T_c and 100 K μ decreases as temperature increases, followed by a region from 100 to 140 K where μ increases with increase in temperature; subsequently, between 140 and 300 K, μ decreases with increase in temperature. Thus, we can see that the variations of n and μ follow the earlier pattern. Except between T_c and 40 K, almost over the entire range of temperature, μ for the deformed state is lower than that for the undeformed state.

For the deformed state of Bi–Tl we have found that n is essentially constant over the temperature range 12 to 90 K. In this region μ varies approximately as $T^{-1/2}$. This could be due to dislocation scattering. Thus in the case of the deformed state there is an additional scattering due to dislocations (subscript Dis) and one can write

$$\frac{1}{\mu_{\text{eff}}} = \frac{1}{\mu_{\text{DPS}}} + \frac{1}{\mu_{\text{IIS}}} + \frac{1}{\mu_{\text{Dis}}} \qquad (8)$$

In the present case, in this temperature region the only effective scattering mechanism appears to be dislocation scattering. The observed $T^{-1/2}$ dependence of σ follows from the variation of μ with T in this region, where n is effectively constant. For temperatures greater than 90 K, n increases exponentially with temperature and the mobility varies approximately as $T^{-3/2}$. This shows that the mobility is governed by deformation potential scattering in this region. The observed variation of σ with T is consistent with the variation of n and μ in this region.

For the deformed state of Bi–Pb in the region 10 to 90 K, n increases slowly and is effectively constant and μ varies approximately as $T^{-1/2}$. This shows that μ is determined by dislocation scattering in this region. The variation of σ with T from 10 to 90 K follows from the variation of μ with T in this region. For temperatures greater than 150 K, the inverse dependence of σ on T is similar to the variation of σ in the case of the deformed state of Bi–Tl. However, for both the deformed specimens this dependence of σ on T in the high-temperature region can be explained on the basis of the Bloch–Grüneissen theory of lattice scattering.

4. Conclusions

In view of the experimental evidence for the occurrence of activation energies, it would appear that the band structure of bismuth has been affected as a result of doping with appropriate concentrations of thallium or lead. Our results are comparable to the changes brought about in the band structure of bismuth when it is doped with various concentrations of antimony. Antimony forms a complete solid solution with bismuth. These alloys have a continuously changing band structure with concentration without changing the equality of electrons and holes. The electrical properties of single crystals of these alloys have been investigated by Jain [26], Tanuma [27] and Ivanov and Papov [28] and it is now well established that alloys containing antimony at $\geqslant 5$ at % and $\leqslant 40$ at % behave like intrinsic semiconductors with small energy gaps. Though the solubility of either thallium or lead in bismuth is very small, yet the electrical and thermal properties of single crystals of the Bi–Tl and Bi–Pb systems, both in the undeformed and deformed states, are not significantly different from those of Bi–Sb alloys. The similarity may be attributed to the change in the band structure of bismuth due to the distortion of the bismuth lattice. It should be noted that the results of the measurements of carrier concentration and the thermal conductivity of Bi–Tl and Bi–Pb in the deformed state are not basically different from those in the undeformed state; only the band gaps have been modified.

Plastic deformation has affected both n and μ of the systems. In the case of Bi–Tl in the deformed state, there is no evidence for the activation energy of 14 meV observed for the undeformed state in the low-temperature region, but the band gap of 40 meV obtained from our observations in the high-temperature region has increased to 90 meV. Similarly, in the case of Bi–Pb the band gap of 18 meV has increased to 50 meV. As a consequence of the effect of plastic deformation on n and μ, the conductivity σ changes accordingly. Thus, plastic deformation plays a significant role in changing the electrical properties of solids.

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