Explanation of the conductivity minimum in tin- and tellurium-doped bismuth

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(Received 23 May 1994)

The presence of a minimum observed in the variation of conductivity of bismuth with impurity concentrations at a constant temperature (4.2 K) has remained unexplained for a long time. An attempt to explain this anomalous behavior is reported here. In order to do so, a calculation has been made to find the change in the number of free carriers in bismuth with the addition of impurities (donors or acceptors). The calculation has been made using simple parabolic bands. It is known that when tin or tellurium atoms are added as impurities to bismuth all of the atoms are ionized. It has been found here that the number of free carriers initially shows a slow rate of decrease (for donors) or a slow rate of increase (for acceptors) as the impurity concentration is increased, as long as the impurity concentration is small, i.e., as long as the shift of the Fermi level is small. For a higher impurity concentration the number of carriers increases at a rate equal to that of the impurity concentration. This finding, combined with the scattering by impurity ions, could explain the anomalous behavior satisfactorily.

INTRODUCTION

Bismuth with overlapping bands is a substance that has interested many workers studying the transport properties of solids.[1–5] Recently, several bismuth-containing oxides have been found to be high-T_c superconducting material.[6–8] Bismuth-antimony alloys have applications in peltier cooling modules and in infrared detectors. An earlier observation was made by Tanaka[1] and later by Van Goor[2] on the variation of the electrical conductivity (σ) of bismuth with the addition of impurities at 4.2 K. They observed that, in the case of impurities which were either acceptors or donors, σ initially decreased to a minimum value and then increased as the concentration (N_i) of impurity centers increased. But when the impurity was neither an acceptor nor a donor, σ decreased with the increase of impurities.

So far, no attempt has been made to explain the appearance of such a minimum in impurity-doped bismuth. It would be of interest to see whether the presence of this minimum is characteristic of bismuth or is observable in all metals with overlapping bands. An attempt has been made in this paper to explain this anomalous behavior of the conductivity with the addition of impurities in bismuth and in solids with overlapping bands in general.

A saturation or a minimum in the temperature variation of electrical conductivity has been observed in metals with high resistivity ($\sim 100\ \mu\Omega$ cm).[9] This phenomenon has been explained[10] to be due to (i) a failure of the Boltzmann theory and (ii) the possibility of an appearance of modes of conduction assisted by interband effects. Both, however, are effects of large scattering and are negligible when the scattering is small. This scattering may be caused either by temperature or by impurity.

In the present case of bismuth, the experimental results have been obtained at 4.2 K and the percentage of impurity confined to within 0.05% (Ref. 1). As a result, the scattering due to both temperature and impurity are rather small.

I. THEORETICAL DISCUSSION

When conduction and valence bands overlap, equal numbers of electrons and holes are produced as free carriers which remain present at all temperatures. Transport properties of such solids will be exhibited by (i) electrons in the conduction band and (ii) holes in the valence band. A schematic diagram of the positions of energy bands in such a solid is shown in Fig. 1. E_F^0 represents the Fermi energy of the pure substance.

When an acceptor impurity is added to such solids the impurity takes electrons from both of the overlapping bands, thereby increasing the number of holes and decreasing the number of electrons. As a consequence, the Fermi level (FL) moves to the left to a position E_F^1, de-

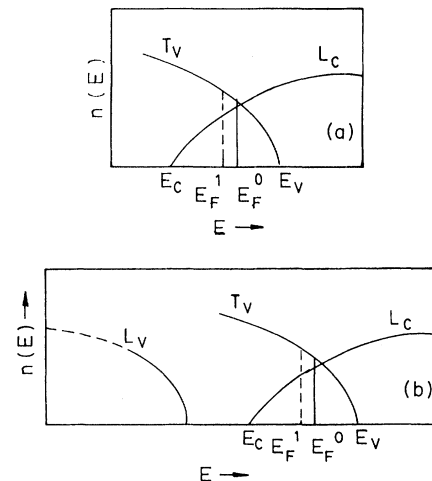

FIG. 1. (a) A general case of two overlapping bands, T_v (valence band) and L_c (conduction band); E_F^0—position of Fermi level in an undoped sample; E_F^1—position of Fermi level when doped with acceptor; E_c—conduction-band minimum; E_v—valence-band maximum. (b) Two overlapping bands of bismuth; L_v—the second valence band.

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pending on the concentration of impurity (see Fig. 1). In the case of a donor impurity, the electrons will increase and the holes decrease in number and the Fermi level will move to the right.

The electrical conductivity σ of a substance depends on the number of free carriers and their mobility at the temperature under consideration. At any constant temperature, to study how σ varies with the percentage of impurity, one has to know the nature of the variation of the concentration of free carriers and the amount of scattering suffered by the carriers.

A. Relation among free carriers, impurity concentration, and shift of Fermi level

For a solid with overlapping bands, we may write (referring to Fig. 1 and assuming a parabolic relation)

$$n_v(E)=C_1(E_v-E)^{1/2} , \quad (1)$$

$$n_c(E)=C_2(E-E_c)^{1/2} , \quad (2)$$

where $n_v(E)$ is the density of states in the T_V band, $n_c(E)$ is the density of states in the L_C band, E_v is the uppermost available energy in the T_V band, and E_c is the lowermost available energy in the L_C band.

If N_0^h and N_0^e represent the number of holes and electrons in bands T_V and L_C, respectively, we then have

$$N_0^h \propto \int_{E_F^0}^{E_v} C_1(E_v-E)^{1/2}dE=C_{11}(E_v-E_F^0)^{3/2} , \quad (3)$$

$$N_0^e \propto \int_{E_c}^{E_F^0} C_2(E-E_c)^{1/2}dE=C_{22}(E_F^0-E_c)^{3/2} . \quad (4)$$

The total number of carriers is

$$N_0^h+N_0^e=\{C_{11}(E_v-E_F^0)^{3/2}+C_{22}(E_F^0-E_c)^{3/2}\} . \quad (4a)$$

When acceptor impurity is added, electrons from both bands T_V and L_C will go to the impurity levels and, consequently, the Fermi level will move to the left of E_F^0 to position E_F^1 (Fig. 1) and the impurity atoms will be ionized. If donor impurity is added, electrons will be donated to both bands T_V and L_C and the Fermi level will, consequently, move to the right of E_F^0 (with reference to Fig. 1). As a result, in this case (donor impurity), electrons in band L_C will increase and holes in T_V will decrease in number. The carriers in bands T_V and L_C will become

$$N_i^h=\int_{E_F^1}^{E_v} C_1(E_v-E)^{1/2}dE=C_{11}(E_v-E_F^1)^{3/2} , \quad (5)$$

$$N_i^e=\int_{E_c}^{E_F^1} C_2(E-E_c)^{1/2}dE=C_{22}(E_F^1-E_c)^{3/2} . \quad (6)$$

The number of holes in T_V will be increased or decreased by ΔN_i^h and the number of electrons in L_C will be decreased or increased by ΔN_i^e, depending on whether the impurity is an acceptor or a donor. The total number of impurities added will be

$$N_{\rm imp}=|\Delta N_i^h|+|\Delta N_i^e| .$$

We may, therefore, write

$$N_{\rm imp}\equiv\pm[(N_i^h-N_0^h)+(N_0^e-N_i^e)] = \pm[C_{11}(E_v-E_F^1)^{3/2}-C_{22}(E_F^1-E_c)^{3/2}] . \quad (7)$$

The negative sign is for the case of donor impurity. The above expressions (5)–(7) relate the concentration of impurities and the number of free carriers with the consequent shift of the Fermi level.

B. Conductivity

The expression for conductivity of the pure solid is

$$\sigma_0=N_0^h e\mu_0^h+N_0^e e\mu_0^e=N_0(\mu_0^h+\mu_0^e) , \quad (8)$$

where N_0^h and N_0^e are the concentrations of holes and electrons and μ_0^h and μ_0^e are their mobilities and $N_0^h=N_0^e=N_0$,

$$\mu_0^h=\frac{e\tau_0^h}{m_h} , \text{ and } \mu_0^e=\frac{e\tau_0^e}{m_e} .$$

τ_0^h and τ_0^e are the respective relaxation times, and m_h and m_e are the effective masses of holes and electrons. If impurity is added now, the expression for conductivity becomes

$$\sigma_i=(N_i^h e\mu_i^h+N_i^e e\mu_i^e) . \quad (9)$$

N_i^h and N_i^e are concentrations of carriers in the doped sample. Here,

$$\mu_i^h=\frac{e\tau_{\rm av}^h}{m_h} \text{ and } \mu_i^e=\frac{e\tau_{\rm av}^e}{m_e} , \quad (9a)$$

where

$$\tau_{\rm av}^h=\frac{1}{\frac{1}{\tau_0^h}+\frac{1}{\tau_i^h}} \text{ and } \tau_{\rm av}^e=\frac{1}{\frac{1}{\tau_0^e}+\frac{1}{\tau_i^e}} , \quad (9b)$$

and $1/\tau_i^h$ and $1/\tau_i^e$ are the scattering due to impurities.

In order to find the values of σ_i [cf. Eq. (9)], the scattering suffered by the carriers should also be known. Since the impurities are ionized, $\tau_i^{e,h}$ can be calculated from the relation[11]

$$\tau_i^{e,h}=\frac{64\pi^{1/2}\epsilon^{1/2}(2kT)^{3/2}}{N_{\rm imp}z^2e^4} \times m_{e,h}^{1/2}\ln\left[\left\{1+\left[\frac{12\pi\epsilon kT}{Ze^2N_{\rm imp}}\right]^2\right\}\right]^{-1} , \quad (10)$$

where Z is the atomic number of the impurity, $m_{e,h}$ are the effective masses of electrons and holes in the host solid, and ϵ is the permittivity. Substituting these values in the expression for conductivity [Eq. (9)], we get

$$\sigma_i=N_i^h e\mu_i^h+N_i^e e\mu_i^e = \frac{C_{11}(E_v-E_F^1)^{3/2}e^2}{m_h\left[\frac{1}{\tau_0^h}+\frac{1}{\tau_i^h}\right]}+\frac{C_{22}(E_F^1-E_c)^{3/2}e^2}{m_e\left[\frac{1}{\tau_0^e}+\frac{1}{\tau_i^e}\right]} . \quad (11)$$

From the above expression, if we want to estimate the

TABLE I. Constants for pure bismuth.

$\sigma_0 = 1.4\times10^6\ (\Omega\,\text{cm})^{-1}$ (Ref. 1)
$(E_F^0 - E_c) = 0.0177$ eV (Ref. 1)
$(E_v - E_F^0) = 0.0117$ eV (Ref. 1)
$N_0 = 2.75\times10^{17}\ \text{cm}^{-3}$ (Ref. 12)
$m_e = 0.05m_0$ (Ref. 13)
$m_h = 0.1m_0$ (Ref. 13)

variation of conductivity (σ) with impurity, we shall have to consider the two terms of the right-hand side of Eq. (11) separately for acceptor and donor impurity. For acceptor impurity (like Pb, Sn), since E_F^1 approaches E_c as impurity concentration increases, and τ_i decreases, the second term, therefore is a decreasing function. In the first term, the numerator increases and the denominator also increases, so the expression might have a chance of increasing, at least when $E_V - E_F^1$ becomes large. The reverse is the case for donor impurity. So whether the value of σ_i will increase or decrease will depend on the magnitude of increase and decrease of the two terms of the right-hand side of Eq. (11). From the above expression, an initial decrease of σ followed by an increase is expected as impurity concentration increases. In the following discussion, we have analyzed Eq. (11) to explain the conductivity minimum obtained in doped bismuth.

II. DISCUSSION

A. Application to bismuth

Since our aim is to find the effect of the concentration of impurities on σ, we make use of the values of $N_0^{e,h}$, etc., for pure bismuth as shown in Table I and proceed to find the dependence of σ_i on N_{imp} at 4.2 K. At this temperature, we do not expect any excitation of carries from L_V and so the free carries of bismuth will be confined to the overlapping bands only. Thus for pure bismuth, the following values at 4.2 K are used. We also assume that at 4.2 K for pure bismuth, $\tau_0^h = \tau_0^e$. Utilizing these values and using the expressions (3)–(10), we can now calculate the values of σ_i, $N_i^{e,h}$, N_{imp} at 4.2 K. $\tau_0^{e,h}$ has been calculated using the relation (10). The dependence of N_i (holes + electrons) on N_{imp} is shown in Fig. 2 (curve 1). The curve (Fig. 3(a), Sn doped) shows that σ_i initially decreases, reaches a minimum, and then increases. This is because the initial slow increase in the number of free carriers (N_i) is not enough to overcome the increase in impurity scattering. Then when the rate of increase of N_i is larger due to the fast increase of holes, σ_i increases.

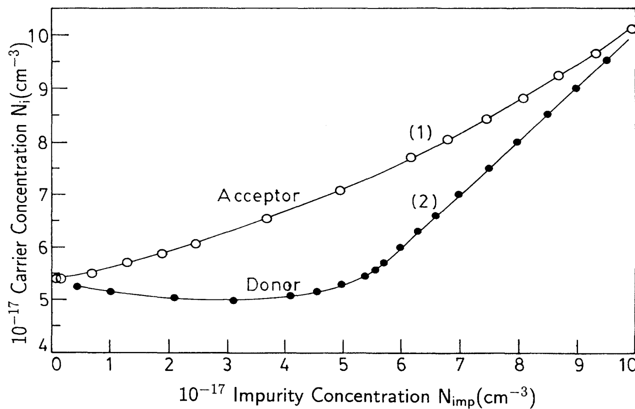
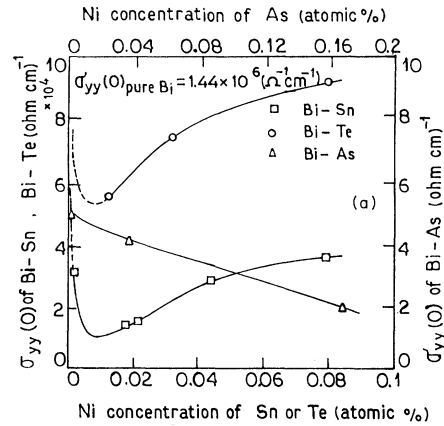
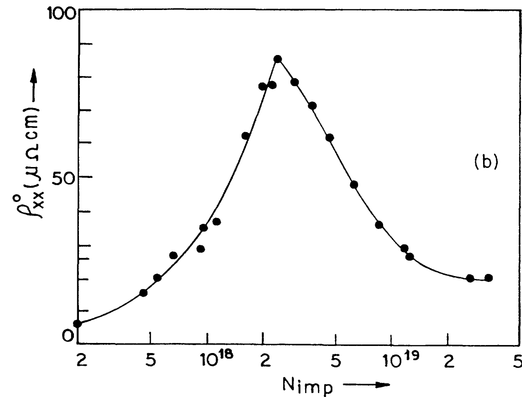


FIG. 2. Calculated variation of concentration of free carries (N_i) with a concentration of impurity: (1) acceptor and (2) donor.





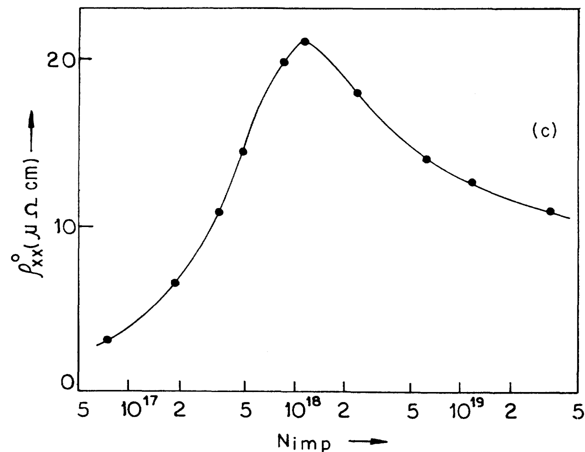


FIG. 3. (a) σ vs N_i curve [reproduced from Tanaka (Ref. 1)], (b) ρ vs N_i [reproduced from Van Goor (Ref. 2)], (c) ρ vs N_i [reproduced from Van Goor (Ref. 2)].

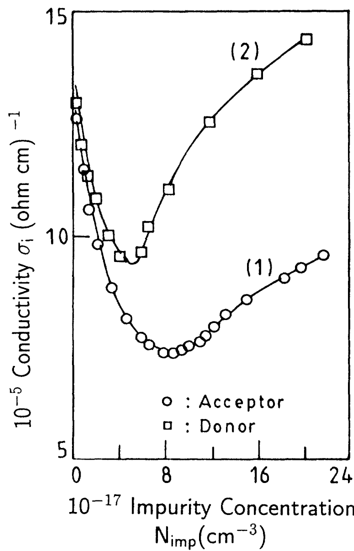


FIG. 4. Calculated variation of conductivity (σ_i) with a concentration of impurity (N_{imp}) (calculated).

The calculated curve (Fig. 4, curve 1) closely resembles the experimental observation[1] [Fig. 1(a)]. It is interesting to note that the minimum occurs before E_F^1 crosses E_c.

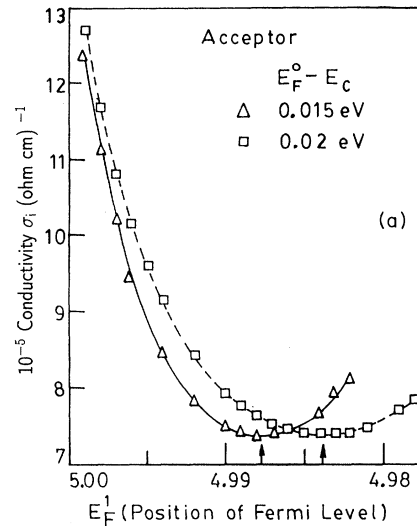
A similar calculation has been made for donor impurities. The variation of N_i (total number of free carriers, i.e., holes + electrons) with N_{imp} can be divided into three regions: (1) N_i initially shows a slight decrease with N_{imp} and then (2) slowly increases where the increase of N_i is less than the increase in N_{imp}, then (3) the increase is more rapid, ultimately making the increase in N_i equal the increase in N_{imp} (Fig. 2, curve 2). Here, also, the curve σ_i vs N_{imp} shows a minimum which occurs before E_F^1 crosses E_V. But, here, the rate of decrease and increase is more rapid than in the case of acceptor impurity (Fig. 4, curve 2). This is because the decrease in σ_i is caused by the initial decrease in the number of free carriers (Fig. 2, curve 2) and the increase in impurity scattering, and the increase in σ_i, by the increase in more mobile electrons. Here, also, the calculated curve (Fig. 4, curve 2) resembles closely the experimental observation[1] [Fig. 1(a)].

B. The effect at ordinary temperature

At ordinary temperature, the acoustic-phonon scattering is much larger than impurity scattering and so the scattering may be considered to be due to phonons only, which will be constant at any particular temperature. Therefore, the variation of σ_i with impurity will assume the nature of variation of N_i with N_{imp} (Fig. 2). The minimum value of σ_i will almost be equal to σ_0 at the ordinary temperature after which σ_i will show a rise. However, this cannot be verified because experimental observations on a solid where carriers are confined to two overlapping bands only are not available. In the case of bismuth where results of such observations are available, the carriers at this temperature do not remain confined to the overlapping bands only and excitation from L_V takes place causing deviation from the above contention.[2]

C. Application to any such solid

We have treated different cases below to see whether even after changing the different parameters of the over-



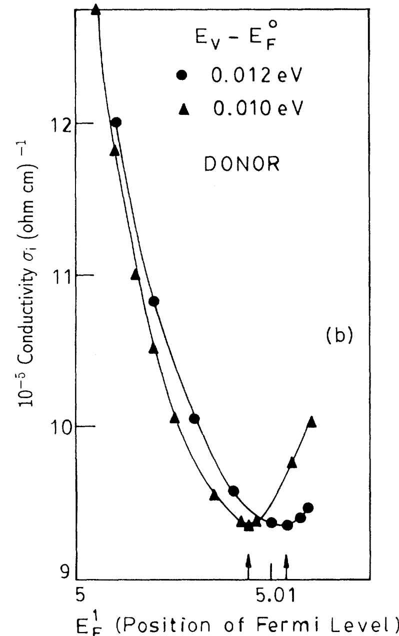


FIG. 5. (a) Calculated variation of σ with a change of E_F^1 (for different values of overlap in the acceptor case):

$$E_v - E_c = 0.024915 \text{ eV} - \triangle$$
$$= 0.03322 \text{ eV} - \square .$$

(b) Calculated variation of σ with a change of E_F^1 (for different values of overlap in the donor case):

$$E_v - E_c = 0.03015 \text{ eV} - \bullet$$
$$= 0.0251 \text{ eV} - \blacktriangle .$$

lapping bands the minimum in the σ_i vs $N_{\rm imp}$ can still be observed. This conclusion applies to the treatment of solids with overlapping bands in general. The following attempts have been made:

(1) Changing the overlap keeping C_{11}, C_{22}, and σ_0 unchanged. As a consequence $N_0^{e,h}$ and $\tau_0^{e,h}$ undergo a change (Fig. 5).

(2) Changing C_{11}, C_{22}, overlap, $N_0^{e,h}$, with consequent change in $\tau_0^{e,h}$. The above considerations show that the σ_0 vs $N_{\rm imp}$ plot always shows a minimum in the case of solids with overlapping bands. The above calculations also show that the position of the conductivity minimum shifts to a larger value of E_F^1, a function of impurity concentration, as the overlap $(E_v - E_c)$ increases [Figs. 5(a) and 5(b)]. Consequently, we examined whether there is any relation between $(E_v - E_c)$ and $N_{\rm imp}$ at $\sigma_{\rm min}$. Though no fixed ratio of the overlap to $N_{\rm imp}$ at $\sigma_{\rm min}$ could be found, it has been found that if we plot σ_i vs E_F^1, the value of E_F^1 at the position of the $\sigma_{\rm min}$ is such that $(E_F^0 - E_F^1)/(E_v - E_c)$ is a constant for different overlaps [where $E_F^0 - E_F^1$ is the shift of (FL) due to the addition of impurities and $E_v - E_c$ is the overlap]. In the case of bismuth, the value of the above-mentioned constant is ~ 0.8 for acceptor impurity (say Sn) and for donor impurity (say Te), this ratio has been found to be $\sim 0.89 (\sim 0.9)$.

CONCLUSION

It may be concluded that the presence of a minimum in the variation of σ_i with impurity concentration is a characteristic of the overlapping band in general. Fitting between calculated and experimental values for Bi [Figs. 4 and 3(a)–3(c)] is not exact. This might be because the values of the parameters N_0, σ_0, etc., used in the calculations are taken from different types of experimental results.

ACKNOWLEDGMENT

One of the authors (D.B.) is thankful to the Council of Scientific and Industrial Research (CSIR), Government of India for financial support.

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