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# Electron scattering in compensated bismuth

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Measurements on the low-temperature variation of the thermopower and thermal and electrical conductivities of pure bismuth and bismuth doped with an equal amount of tin and tellurium are compared. The counter-doped sample behaves as a compensated semimetal combining pronounced impurity scattering together with a Fermi-level characteristic of intrinsic material. If a rigid-band model and the validity of Matthiessen's rule are assumed, the resistivity variation with temperature indicates that the combined effect of the tin and tellurium addition is that of neutral impurity scatterers. The diffusion thermopower is not inconsistent with this observation. The low-temperature phonon-drag hump is negative contrary to pure bismuth which exhibits a positive hump. The lattice thermal conductivity around the maximum is considerably reduced as compared to pure bismuth and the difference persists at higher temperatures.

## I. INTRODUCTION

The simultaneous presence of electrons and holes in bismuth at all temperatures due to overlapping bands[1] stimulated studies on doped material. It was thought that investigating the properties of a single-carrier system would help interpreting the effects observed in the intrinsic material. In fact, it was realized early that, owing to its particular semimetallic structure, the addition of small amounts of tin or tellurium to bismuth would drastically change its electrical properties.[2] However, three decades were necessary to see these exploratory works confirmed quantitatively, with particular emphasis put on the effect of doping on the electronic structure of bismuth.[3,4] Also, the effect on the thermoelectric properties of tin and tellurium separately introduced into bismuth has been systematically investigated.[5] However, doping with either donors or acceptors has important drawbacks, some of them being specific to semimetals. In order to get rid of electrons or holes at 0 K, one needs a tin (acceptor) or tellurium (donor), contents of $4\times10^{18}$ and $8\times10^{17}$ $\text{cm}^{-3}$, respectively,[4] which is rather heavy doping.[6] A change in relaxation times for the doped material with respect to the pure one will result not only from increased impurity scattering, but also from a quantitative change in pure electron-phonon acoustic scattering. Since the main effect of doping is to alter the Fermi level, there will be a change in the Fermi wave vector for charge carriers $k_F$, thus a corresponding change in the maximum wave number of interacting phonons $q_{\max} = 2k_F$ leading to an interaction with phonons of wave numbers different from those which scatter the charge carriers in the intrinsic material.

Furthermore, if a nonparabolic model is assumed for electrons,[1] their effective masses in a given direction will vary with energy according to

$$m^* = m_0^*(1 + 2E/E_g), \tag{1}$$

where $m_0^*$ is the effective mass at the bottom of the band, $m^*$ is the effective mass at the energy $E$, and $E_g$ is the direct energy gap between the bottom of the conduction band and the top of the lower-lying light-hole band. Hence, doping would alter the mobilities at the Fermi level because they depend on the effective mass.

For these reasons, it was thought that it would be interesting if one could perform transport measurements on a compensated sample, i.e., a sample counterdoped in such a way that the Fermi level remains unaltered with respect to the intrinsic material. It was only recently that bismuth single crystals with various and well-defined amounts of tin and tellurium acting simultaneously were successfully grown at the Philips Research Laboratories (Eindhoven) by a method described elsewhere.[4] Noothoven van Goor[4] determined the carrier concentration and mobilities of these doped samples by means of the saturation value of the galvanomagnetic coefficients at low temperatures. Among the crystals investigated was one with an almost equal donor and acceptor concentration, Bi 102, in Ref. 4. The Fermi level of this sample is expected to be the same as in intrinsic material. Here we report measurements on the temperature dependence of some transport properties of this material, and compare them to those obtained with pure bismuth in the same crystallographic orientation.

## II. EXPERIMENTAL

The compensated sample was grown at the Philips Research Laboratories.[4] The sample axis was oriented in the bisectrix direction ($y$ axis), and Noothoven van Goor suggests from his measurements that the total dopant density $N_A + N_D$ lies between $1.8\times10^{18}$ and $3.2\times10^{18}$ cm$^{-3}$, and that the tin concentration $N_A$ exceeds that of the tellurium $N_D$ by an amount $N_A - N_D = 1.45\times10^{16}$ cm$^{-3}$. In the following we shall make ours the generally accepted assumption, i.e., that each tellurium atom is ionized and adds one electron to the Fermi sea, and each tin atom adds one hole. Further, we shall assume $N_A \simeq N_D$. A sample of pure bismuth with its axis in the bisectrix direction and a residual-resistance ratio of 200 was also studied in parallel for comparison.

The samples were mounted in a vertical variable temperature liquid-helium cryostat. The temperature sensors were Au(Fe)-vs-*p*-Chromel thermocouples and the voltage leads consisted of thin *p*-Chromel wires. Emf's were measured by means of a Leeds and Northrup K-5 potentiometer and a sensitive null detector. The system had a resolution better than $10^{-8}$ V. Above the liquid-helium bath the temperature was regulated by means of a Harwell temperature controller. Since the resistivity was measured by a dc method, special care was taken to correct for the Peltier effect,[7] which may be important because of the relatively high figure of merit of the material in the higher-temperature range.

## III. RESULTS

We have examined the electrical resistivity, thermoelectric power, and thermal conductivity as a function of temperature for the compensated sample, and compared them with measurements we performed on pure bismuth in the same temperature range.

The open circles in Fig. 1 give the electrical resistivity measured from 2 to 300 K on the compensated sample. In the lowest-temperature range we find an almost constant resistivity of $108\times10^{-6}$ $\Omega$ cm.[8] Then the resistivity increases with temperature, reaches a maximum, decreases until it reaches a flat minimum, and then increases again with further increase in temperature. The dashed curve represents the electrical resistivity of pure bismuth (residual-resistivity ratio of $\simeq$200), which, at this scale, may be considered to be the ideal one.

In Fig. 2, the open circles represent the measured thermoelectric power from 2 to 300 K on the compensated sample, while the dashed line is the corresponding curve for pure Bi. Contrarily to the case of pure bismuth, the thermoelectric power of the compensated sample is negative in the lowest-temperature range. It shows a hump around 4 K, decreases slightly in magnitude, and then increases again to reach another hump around 120 K.

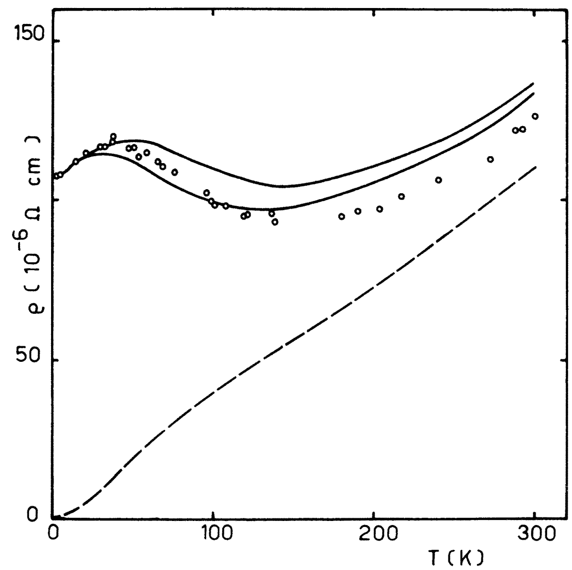


FIG. 1. Temperature dependence of the electrical resistivity of compensated bismuth compared to that of pure bismuth. The dashed curve represents the experimental data for pure bismuth. The open circles are the experimental points measured on the compensated sample, while the two solid lines are the computed curves with two assumptions concerning the carrier density at 0 K ($\sim 3\times10^{17}$ cm$^{-3}$). The upper plain line is computed with $N = 3.28\times10^{17}$ cm$^{-3}$ (Ref. 4) and the lower one with $2.75\times10^{17}$ cm$^{-3}$.

Note too that the magnitude of its thermopower is larger than that of pure bismuth in the entire temperature range.

The thermal conductivity of both samples are also compared in Fig. 3. For pure bismuth the dielectric maximum is sharper and is situated at a lower temperature. Also, in the entire temperature range investigated (2–100 K), the compensated sample shows a lower thermal conductivity.

## IV. DISCUSSION

In the discussion of our results we shall assume a rigid-band model, i.e., that the band structure of compensated bismuth is not affected by doping (same as for pure bismuth), and is independent of temperature. From the recent work of Vecchi and Dresselhaus,[9] we know that this last assumption is not realistic, however we do not yet have quantitative data about the variation of the effective masses of pure bismuth with temperature.

When two types of independent carriers of equal densities $N_e = N_h = N$ of mobilities $\mu$ and $\nu$ and partial thermopowers $\alpha_e$ and $\alpha_h$ are acting simultaneously, they combine to yield for the total elec-

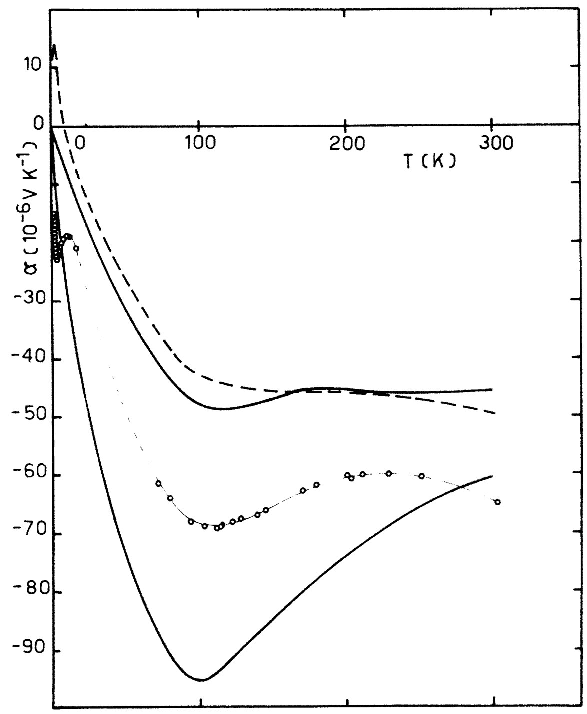


FIG. 2. Temperature dependence of the thermoelectric power of the compensated sample compared to that of pure bismuth. The dashed curve represents the experimental data for pure bismuth. The open circles are the experimental points measured on the compensated sample, while the two solid lines are the computed curves, the upper one corresponding to pure bismuth and the lower one to the compensated sample.

trical conductivity

$$\sigma = Nq(\mu + \nu), \tag{2}$$

as if both types of carriers behave as conductors in parallel, and for the total thermopower,

$$\alpha = (\alpha_e \mu + \alpha_h \nu)/(\mu + \nu), \tag{3}$$

acting as sources in parallel. Here $q$ is the electronic charge, and the subscripts $e$ and $h$ refer to electrons and holes, respectively.

On the other hand, when a set of carriers, say, the electrons, of density $N$, experiences a scattering by two distinct mechanisms characterized by mobilities $\mu_r$ and $\mu_i$ and partial thermopowers $\alpha_r$ and $\alpha_i$, respectively, the electrical conductivity is expressed

$$\sigma_e = Nq(1/\mu_r + 1/\mu_i)^{-1}, \tag{4}$$

as if both resistive mechanisms add. This is the well-known Matthiessen's rule.

In a similar way one may express the resulting thermopower

$$\alpha = \frac{\alpha_r/\mu_r + \alpha_i/\mu_i}{1/\mu_r + 1/\mu_i}. \tag{5}$$

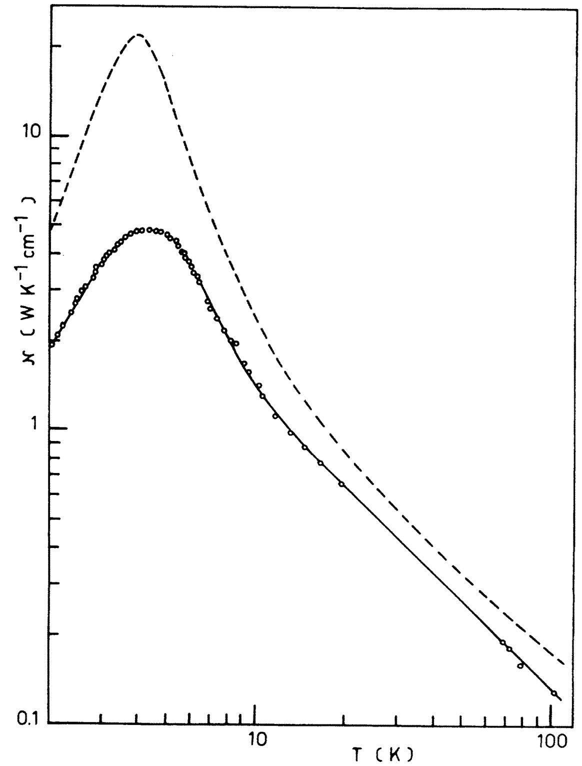


FIG. 3. Measured temperature dependence of the thermal conductivity of the compensated sample (solid line, open circles) compared to that of pure bismuth (dashed line).

This is known as the Gorter-Nordheim rule.

In the case of compensated material we deal with two types of carriers, electrons and holes, in almost equal density. Let us first assume that each type is scattered by two mechanisms of indices $r$ and $i$. The corresponding mobilities of electrons and holes, respectively, are $\mu_r$, $\mu_i$ and $\nu_r$, $\nu_i$, and the partial thermopowers $\alpha_{er}$, $\alpha_{ei}$ and $\alpha_{hr}$, $\alpha_{hi}$. The total electrical conductivity is then

$$\sigma = Nq\left[\left(\frac{1}{\mu_r} + \frac{1}{\mu_i}\right)^{-1} + \left(\frac{1}{\nu_r} + \frac{1}{\nu_i}\right)^{-1}\right], \tag{6}$$

obtained by adding the resistive mechanisms for each type of carriers first, then by adding the contributions of electrons and holes to the total electrical conductivity. By applying the same rule to the partial thermopowers, one finds a total thermoelectric power of

$$\alpha = \left(\frac{\alpha_{er}/\mu_r + \alpha_{ei}/\mu_i}{(1/\mu_r + 1/\mu_i)^2} + \frac{\alpha_{hr}/\nu_r + \alpha_{hi}/\nu_i}{(1/\nu_r + 1/\nu_i)^2}\right) \times \left(\frac{\mu_r\mu_i}{\mu_r + \mu_i} + \frac{\nu_r\nu_i}{\nu_r + \nu_i}\right)^{-1}. \tag{7}$$

In our experimental data being measured in the trigonal plane of bismuth, i.e., the plane that contains the binary and bisectrix axis, $\mu$ and $\nu$ will be the arithmetical average electron and hole mobilities, respectively, between binary and bisectrix mobilities.

### A. Electrical resistivity

The experimental data will be interpreted by means of Eq. (6) over the entire temperature range from 2 to 300 K. The carrier density $N$ will be assumed to equal at each temperature that of pure bismuth.[10] The index $i$ will refer to the scattering by acoustical phonons and $\mu_i$, $\nu_i$, $\alpha_{ei}$, and $\alpha_{hi}$ will be assumed equal to those characteristic of pure bismuth throughout the temperature range, while the index $r$ will refer to the scattering due to the added impurities.

Let us further assume that at the lowest temperatures (2–4 K), $\sigma$ has reached its residual value $\sigma_r$, hence $1/\mu_i \ll 1/\mu_r$, and

$$\sigma \simeq \sigma_r = Nq(\mu_r + \nu_r)\,. \tag{8}$$

This means that with $N = 2.75\times10^{17}$ cm$^{-3}$ (Ref. 11) (Fig. 1), in order to fit the experimental result $\mu_r + \nu_r = 21\times10^4$ cm$^2$ V$^{-1}$ sec$^{-1}$ at low temperature. Moreover, Noothoven Van Goor[4] finds a mobility ratio $\mu_r/\nu_r = 15.6$ from resistivity and Hall effect measurements. If we hold the same ratio, we obtain $\mu_r = 19.7\times10^4$ and $\nu_r = 1.27\times10^4$ cm$^2$ V$^{-1}$ sec$^{-1}$. If we assume, as a first step, that $\mu_r$ and $\nu_r$ are temperature insensitive, since we know the $\mu_i$ and $\nu_i$ temperature dependence,[10] we may, by means of relation (6), compute the total resistivity variation with temperature $\rho(T)$. We find that the computed $\rho(T)$ fits the experimental data well (Fig. 1). From this we may reasonably infer that the underlying assumption is justified, and that in counter-doped compensated bismuth, the tin and tellurium atoms act as some kind of neutral impurity scatterers.

### B. Thermoelectric power

We shall be concerned mainly with the higher temperature range of the thermopower results, and disregard the phonon drag component. In order to compute the diffusion term of the thermopower of pure and compensated bismuth, we shall add to the assumption of a rigid-band model that of parabolic electron and hole bands.[12,13] The variation of the Fermi energy with temperature may be computed from the known density of states and the experimentally determined temperature variation of the carrier density.[10] The value of the Fermi energies at 0 K, which are specified with respect to the energy extrema in the hole and electron carrier pockets, will be taken for holes 12 meV, and for electrons 16 meV. The partial thermopowers will be expressed by the classical formula involving the Fermi-Dirac integrals $F_i(\eta_F)$, where $\eta_F = E_F/k_BT$ is the reduced Fermi energy

$$\alpha = \pm \frac{k_B}{q}\left(\frac{(r+2)F_{r+1}(\eta_F)}{(r+1)F_r(\eta_F)} - \eta_F\right). \tag{9}$$

Here, $r$ is the scattering parameter characterizing the relaxation time energy dependence $\tau = \tau_0 E^{r-1/2}$; for scattering by acoustical phonons $r = 0$ and by neutral impurities $r = \frac{1}{2}$.

Let us first fit the experimental results for pure Bi, applying (9) for electrons and holes, with $r = 0$, then combining them by means of (3) with $\mu = \mu_i$ and $\nu = \nu_i$, the intrinsic mobilities. Surprisingly enough the resulting computed curve is in qualitative agreement with the experimental one at high temperature (Fig. 2).

To be consistent with the resistivity results we now introduce for the compensated sample, the hypothesis of neutral impurity scattering $r = 1/2$ in (9), and the temperature independent impurity scattering mobilities $\mu_r = 19.7\times10^4$ and $\nu_r = 1.27\times10^4$ cm$^2$ V$^{-1}$ sec$^{-1}$ that we used for the computation of $\sigma$. By means of Eq. (7), we obtain the computed solid curve on Fig. 2. This at least accounts for the increase in absolute value of the thermopower of the compensated sample compared to that of pure bismuth, since the higher the value of the scattering parameter, the higher the partial thermopowers. It also accounts for the position of the bump around 100 K.

### C. Thermal conductivity

In the temperature range investigated, the thermal conductivity of bismuth is never of the electronic type exclusively. Between 2 and 20 K, the phonon contribution exceeds by far that of electrons and holes, which could be neglected. Thus the difference in thermal conductivity we observe around the dielectric maximum should be attributed to the reduction of the mean free path of the phonons due to impurity scattering in compensated bismuth. It is worth noting, however, that a quantitative comparison could not be done, since in this temperature range, and even above 40 K, the lattice thermal conductivity is known to be size dependent.[14] At higher temperatures the electronic thermal conductivity increases and should be affected by impurity scattering in the compensated sample, as it is the case for the electrical conductivity. This would probably explain the difference between the two curves at the higher temperatures.

It is interesting to note that from Figs. 1 and 2, and a reasonable extrapolation of the data of Fig. 3, the temperature variation of the thermoelectric figure of merit ($\alpha^2\sigma/\kappa$) can be estimated. Although still too low to be of interest for practical applications, it is worth noting that above 150 K this parameter is twice as large in the compensated material than it is in the intrinsic one.

## V. CONCLUSIONS

We have initially studied compensated bismuth in order to investigate the effects of doping under simplified conditions, i.e., to test the effect of impurities on the scattering parameter of electrons and holes with Fermi energies and wave vectors of interacting acoustical phonons identical to those in the intrinsic material. However, starting from the experimental observations of the electrical resistivity, it was apparent that this would not be the case. It was found that the study of the compensated material complicated rather than simplified the situation.

In fact, if the simplifying assumptions of a rigid-band model and fulfillment of Mattheissen's rule are valid, the present results are consistent with the fact that the addition of tin and tellurium in almost equal density introduces a temperature independent scattering mechanism for electrons and holes. Such a mechanism is characteristic of neutral impurity scattering, and would thus suggest that tin and tellurium behave in the bismuth matrix as a kind of neutral complex, at least as far as it is viewed from the long wavelength Fermi electrons and holes which are scattered. This may be a challenging problem for metallurgists to elucidate.

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