# High-Precision, Ultralow-Temperature Resistivity Measurements on Bismuth

C. Uher and W. P. Pratt, Jr.
*Department of Physics, Michigan State University, East Lansing, Michigan 48824*
(Received 27 June 1977)

We report the first ultralow-temperature resistivity measurements on Bi with a precision better than 0.01% using a superconducting quantum interference device null detector. The results are inconsistent with simple carrier-carrier scattering. A Bloch-Grüneisen formula for electron-phonon scattering gives an approximate fit to the lowest-temperature data with an effective reduced Debye temperature of the order of 2 K.

There has been recent controversy concerning the nature of the electron-scattering mechanism which determines the temperature dependence of the electrical resistivity of Bi at low temperatures. Previous studies[1-5] have shown that in the temperature interval 1.3–4 K the electrical resistivity of bismuth varies quadratically with temperature. This behavior has been attributed to either charge-carrier–phonon scattering[6,7] or carrier-carrier scattering.[3,8] However, no clear-cut choice in favor of either theory has been possible because of the narrow temperature interval experimentally covered and the low precision of the measurements. Most recently Kukkonen and Maldague[9] have solved the coupled electron and hole Boltzmann equations and obtained an explicit expression for the coefficient of the $T^2$ resistivity term for a degenerate semimetal due to electron-hole scattering. They subsequently applied the theory to bismuth[10] and obtained excellent agreement with the experimental values of Fenton *et al.*[3] and Chopra, Ray, and Bhagat.[4] According to their theory, and in fact any simple carrier-carrier scattering theory, the resistivity of Bi should continue to decrease as $T^2$ with the same coefficient at still lower temperatures. We have made the first ultralow-temperature measurements to see whether this occurs. We state at the outset that our results are not consistent with a simple $T^2$ behavior below 1.6 K.

A superconducting quantum interference device (SQUID) null detector was used to obtain resistivity data with a precision in the range of 0.001% to 0.01%. Such high precision is required to resolve the small temperature-dependent part of the total resistivity at the lowest temperatures. In order to eliminate magnetoresistance effects on the scale of our precision, measuring currents were kept below 0.5 mA and the ambient magnetic field was reduced by Mumetal shielding to 0.5 $\mu$T. The geometric factor for each sample which is used in computing the resistivity has an uncertainty of 1%.

The experiments were performed in a locally constructed dilution refrigerator[11,12] on samples made from 99.9999% purity Cominco bismuth. Four of these were single crystals grown by a technique similar to one described elsewhere.[13] In addition a fine-grain polycrystalline sample was prepared by rapid quenching from the melt. Some of the sample properties are given in Table I. Two superconducting voltage probes were soldered to the side of each rod-shaped sample, typically 8 cm apart and at least five sample diameters away from the superconducting current leads attached at the ends of the sample. For samples

TABLE I. Experimental parameters for Bi samples. The orientations of the single crystals refer to the angle between the trigonal axis and the sample axis. The residual resistivity $\rho_0$ is taken as the value of $\rho$ at the lowest experimental temperatures. Parameters $A$ and $\theta_D^*$ are defined by Eq. (1).

| Sample | Diameter (cm) | Orientation | Surface | $R_{300}/R_{4.2}$ | $\rho_0$ ($\mu\Omega$ cm) | $A$ ($\mu\Omega$ cm) | $\theta_D^*$ (K) |
|---|---|---|---|---|---|---|---|
| Bi No. 1 | 0.35 | 85° | etched | 205 | 0.4258 | 0.113 | 1.99 |
| Bi No. 2 | 0.23 | 90° | etched | 190 | 0.4591 | 0.151 | 2.24 |
| Bi No. 3 | 0.30 | 49° | etched | 190 | 0.5400 | 0.112 | 1.82 |
| Bi No. 4 | 0.44 | Polycrystal | etched | 40 | 2.883 | 0.198 | 2.58 |
| Bi No. 5 | 0.43 | 79° | as grown | 370 | 0.1848 | 0.058 | 1.37 |

Nos. 1 and 2 soft solder was used, and for the remaining samples Cerrolow 117 was employed. Sample No. 4 was cast with protruberances on it which separated the two soldering points from the main axis of the sample by two sample diameters. Such variations in voltage-probe attachments were done in order to see if a current-dependent resistivity was induced by the uncontrolled formation of various superconducting alloys of Bi at these soldering sites. We have varied the magnitude and polarity of the measuring current for all samples and have not observed any current dependence on the scale of our precision. Our measurements[14] of the thermopower and the thermal conductivity of these samples indicate that systematic errors in the resistivities due to the Peltier effect are of the order of 0.001% above 0.2 K and substantially smaller below.

In Fig. 1 we show the overall temperature dependence of the resistivity of the Bi samples. For comparison, the dashed line indicates the data of Chopra, Ray, and Bhagat[4] for a sample of similar quality. Straight lines with slopes in the range $(7.7\pm0.5)\times10^{-9}$ Ω cm $K^{-2}$ fit the data for all single-crystal samples in the region of 1.6–4.5 K. The polycrystalline sample shows a similar behavior but with the straight-line region shifted to approximately the 3–5 K interval. At about 1.6 K, there appears a marked break in the resistivity curves for all the samples. This break has not been seen before, presumably because it occurs around the lower limit of the previously explored temperature interval and also because previous resistivity measurements were much less precise.[15]

The temperature interval below 1 K is expanded in Fig. 2. A quadratic temperature dependence is clearly the best integer-power fit to all the data, but below approximately 0.3 K we observe significant deviations from this behavior. These deviations are better illustrated in Fig. 3, where the dashed-dot curves represent extrapolations of $T^2$ fits to the data in the temperature interval from 0.3 to 0.7 K. The deviations are several times larger than the uncertainty in our measurements.

Our measurements reveal three phenomena which are at variance with simple carrier-carrier scattering: First, there is a distinct break in the slopes of the $T^2$ plots near 1.6 K which results in slopes below 1 K nearly twice as large as those estimated by Kukkonen and Maldague for electron-hole scattering. Second, although the $T^2$

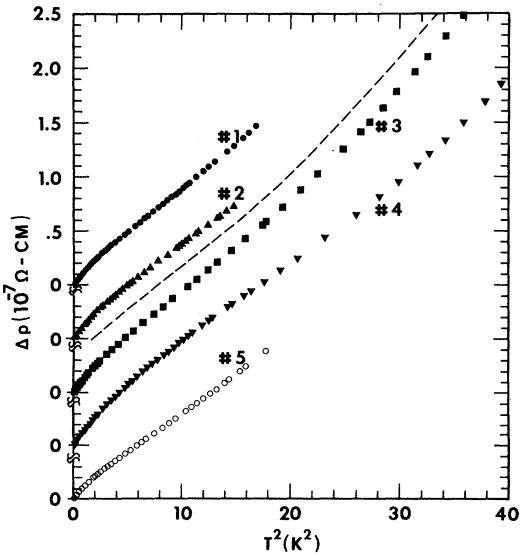


FIG. 1. The temperature-dependent resistivity $\Delta\rho = \rho(T) - \rho_0$ plotted against $T^2$. A common scale is used for all the samples. The dashed curve represents the data of Chopra, Ray, and Bhagat (see Ref. 4) with arbitrarily chosen $\rho_0$ for display purposes.

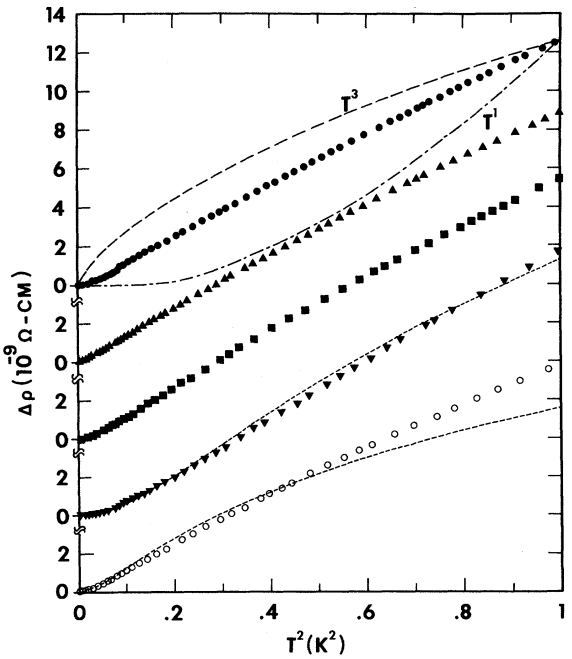


FIG. 2. The temperature-dependent resistivity plotted against $T^2$. A common scale is used for all the samples. The symbols refer to the same samples as in Fig. 1. The dashed and dot-dashed curves present the data of sample Bi No. 1 plotted against $T^3$ and $T$, respectively. The dashed curves for Bi No. 4 and No. 5 are representative fits of Eq. (1) to the data with parameters given in Table I.

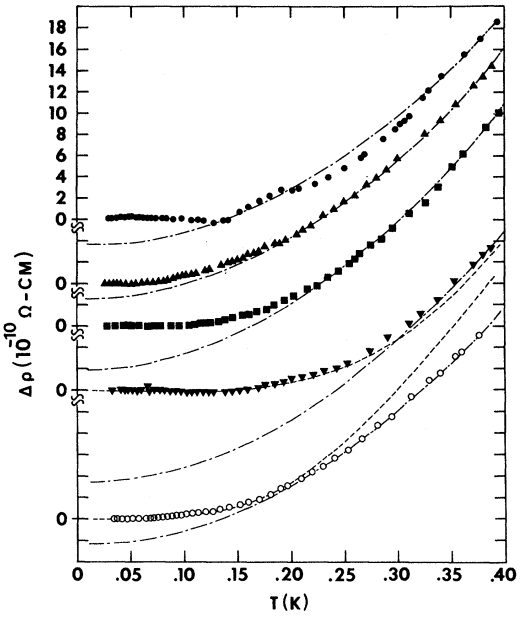


FIG. 3. Temperature-dependent resistivity plotted against $T$. The symbols represent the same samples as in the previous graphs. Again, a common scale is used for all the samples. The dot-dashed curves are extrapolated $T^2$ variations, and the dashed curves for samples Bi No. 4 and Bi No. 5 are representative fits with Eq. (1).

law appears to be the best integer-power fit to the resistivity data over limited temperature intervals, our high-precision measurements demonstrate that it is in fact impossible to fit the data to any power law of the form $\Delta\rho = \gamma T^x$ over the whole temperature range up to 4 K. Last, and perhaps most important, the limiting residual resistivity is attained at relatively high temperatures, suggesting that a much higher exponent in the power law than the one traditionally associated with the carrier-carrier scattering mechanism is responsible for the temperature dependence of the resistivity below 0.3 K.

We have, therefore, attempted to fit the experimental data with the simplest form of electron-phonon scattering as described by the Bloch-Grüneisen formula,

$$\Delta\rho = A\left(\frac{T}{\theta_D}\right)^5 \int_0^{\theta_D/T} \frac{z^5 dz}{(e^z-1)(1-e^{-z})}, \qquad (1)$$

where $\theta_D$ is the Debye temperature. Because of energy and momentum conservation, an electron can interact only with phonons whose wave vectors are not larger than the maximum dimension of the Fermi surface (we ignore intervalley scattering). As the carrier pockets in Bi are very small,[16] the effective phonon cutoff is not determined by the true Debye temperature ($\theta_D = 120$ K) but a reduced Debye temperature $\theta_D^*$—the fact pointed out by Sondheimer.[17] The Bloch-Grüneisen formula may seem, at first, hopelessly inadequate to describe the electron-phonon scattering in Bi with its multivalley, highly anisotropic ellipsoidal Fermi surfaces (semi-axes ratio 1:1.3:15). However, at very low temperatures, electrons will be scattered through small angles only, and as the main contribution to the temperature dependence of resistivity comes from the region of light effective mass, the Bloch-Grüneisen formula in this case should be an adequate approximation. Under such conditions we expect that $\theta_D^*$ will correspond to the minimum dimension of the Fermi surface and thus be of the order of 1 K.

We have determined parameters $A$ and $\theta_D^*$ using a $\chi^2$ fit of Eq. (1) to our experimental data below 1 K. The results are presented in Table I. The values of $\theta_D^*$ are in agreement with expectations, despite the crudeness of the model and the use of Eq. (1) near 1 K where it may cease to be a satisfactory approximation because of large-angle scattering. The predictions of Eq. (1) are in excellent agreement with the experimental data for the polycrystalline sample No. 4 and are not inconsistent with the data for single-crystal samples; the least satisfactory agreement is illustrated for sample No. 5 by the dashed curves in Figs. 2 and 3.[18,19]

We conclude that to consider carrier-carrier scattering as the dominant contribution to the temperature-dependent resistivity of Bi is not consistent with our ultralow-temperature measurements. Despite its obvious shortcomings, electron-phonon scattering as described by a simple Bloch-Grüneisen formula reflects the most important features observed experimentally at the lowest temperatures. We hope that these new results will stimulate further theoretical developments.

We are grateful to Dr. J. Opsal for many valuable comments and help with the computer data fitting. We are also indebted to Professor F. J. Blatt and Professor J. Bass for a critical reading of the manuscript and most helpful suggestions. This work was supported by the National Science Foundation, Grant No. DMR-75-01584.

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[18]The difference between the predictions of the Bloch-Grüneisen formula and an extrapolation of the $T^2$ resistivity variation between 0.3 and 0.7 K is only about $3\times10^{-9}\ \Omega$ cm, even at temperatures as high as 1 K. Unless the measurements are done with a much better precision than 1%, one could not distinguish between the two mechanisms.
[19]Since Eq. (1) is presumed valid only at the lowest temperatures, the agreement between predictions of Eq. (1) and the data for single-crystal samples can be improved by making a fit to the data at lower temperatures, say, below 0.6 K. As a consequence, $\theta_D{}^*$ is reduced by about 20%. We have also attempted to include the anisotropy of the Bi Fermi surface in the electron-phonon scattering, along the lines suggested by Cheremisin (Ref. 6). Below 1 K we have done a computer fit to the expression

$$\Delta\rho = A\left(\frac{T}{\theta_{\min}{}^*}\right)^5 \int_0^{\theta_{\min}{}^*/T} \frac{x^5\,dx}{(e^x-1)(1-e^{-x})} + B\left(\frac{T}{\theta_{\min}{}^*}\right)^n \int_{\theta_{\min}{}^*/T}^{\theta_{\max}{}^*/T} \frac{x^n\,dx}{(e^x-1)(1-e^{-x})},$$

where $\theta_{\min}{}^*$ and $\theta_{\min}{}^*$ are temperatures corresponding to the minimum and maximum dimensions of the Fermi surface, and $n$ is an integer. We have tried $n = 2, 3$. However, we were unable to achieve a significant improvement of the fits to the data below 1 K unless the coefficient $B$ was chosen to be an order of magnitude smaller than the coefficient $A$.

# Anomalous Electrical Transport Properties of $Ni_{1-x}Co_xS_2$

A. K. Mabatah and Ellen J. Yoffa
*Department of Physics, Center for Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139*

and

P. C. Eklund, M. S. Dresselhaus, and David Adler
*Department of Electrical Engineering and Computer Science, Center for Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139*

(Received 19 May 1977)

We report results of electrical conductivity and thermoelectric power measurements on $Ni_{1-x}Co_xS_2$ ($0 \le x \le 0.12$) in the temperature range 77 K$<T<$ 600 K. When analyzed on the basis of conventional one-electron theories, these results are difficult to explain. However, the measurements can be quantitatively interpreted in terms of a model involving polaron transport in highly correlated, narrow energy bands associated primarily with the transition-metal cations.

The transport properties of the 3*d* transition-metal dichalcogenides having the pyrite structure have been intensively studied, but are still incompletely understood.[1,2] Previous workers have inferred an energy-level scheme in which the levels relevant to transport form a narrow antibonding band associated primarily with the 3*d* $e_g$ states of the metal cations.[1] To explain the semiconducting properties of $NiS_2$, it has been speculated that $NiS_2$ is a Mott insulator, that is, insulating as a result of strong interelectronic correlations in this narrow band.

In this Letter, we present experimental results of transport measurements on the alloys