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Low temperature magnetoresistance measurements on bismuth nanowire arrays

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Abstract

We present low temperature resistance $R(T)$ and magnetoresistance measurements for Bi nanowires with diameters between 100 and 500 nm, which are close to being single-crystalline. The nanowires were fabricated by electrochemical deposition in pores of polycarbonate membranes. $R(T)$ varies as T^2 in the low temperature range $1.5\ \mathrm{K} < T < 10\ \mathrm{K}$ and exhibits a maximum which shifts from 140 to 250 K with decreasing wire diameter. An unexpected effect is observed in $R(T)$ when a magnetic field is present. It can be related to the temperature dependence of the magnetoresistance. The transverse magnetoresistance of all samples shows a clear $B^{1.5}$ variation. Its size depends strongly on the diameter of the wires but only weakly on temperature. Finally, a steplike increase in the magnetoresistance of our sample with a wire diameter of 100 nm was found and this might be attributed to a transition from one-dimensional to three-dimensional localization.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Nanowires have been studied extensively over the past few years, not least because of their possible future applications, such as electronic, sensory or thermo-electric devices. In particular, bismuth wires have been widely investigated due to the unique electronic properties of this element. Being a semi-metal with a very small indirect band-overlap (38 meV at 0 K) Bi has a temperature dependent electron density n ($3 \times 10^{18}\ \mathrm{cm}^{-3}$ at 300 K, $3 \times 10^{17}\ \mathrm{cm}^{-3}$ at 4 K), which is four to five orders of magnitude lower than that of ordinary metals. As phonon scattering causes the mobility to depend on temperature, a non-monotonic resistance over temperature behaviour can occur, which is usually attributed to an additional limitation of the mean free path by temperature independent boundary scattering [1, 2]. The Fermi surface of Bi consists of ellipsoidal pockets for electrons and holes, resulting in small effective masses m_{eff} (as low as $0.001 m_{\mathrm{e}}$) and large Fermi wavelengths λ_{F} (~40 nm). Mean free paths l_{e} are as long as ~100 nm at 300 K and ~400 μm at 4 K. These last properties make Bi nanowires an interesting object for studies of quantum size effects. Moreover, a metal–semiconductor transition and an enhanced thermo-electric figure of merit has been predicted [3] and largely verified [1, 4] for diameters smaller than ~50 nm.

In the present paper we report electric transport measurements of arrays of Bi nanowires with diameters between 100 and 500 nm. Samples were nearly single-crystalline and of very high quality as demonstrated by unusually high residual resistivity ratios. Our experiments allow the extraction clear functional relations of the resistance on diameter, temperature, and magnetic field.

2. Sample fabrication and characterization

Bismuth nanowires with diameters of 100, 150, 350 and 500 nm were fabricated by electrochemical deposition in ion

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Table 1. Overview of the measured bismuth nanowire arrays. The irradiated area was approximately 0.5 cm^2.

Diameter (nm)	Fluence (μm^{-2})	R at 295 K (Ω)	Number of wires
500	0.1	0.028	~17 200
350	0.1	1.51	~650
150	1	6.28	~850
100	1	168.7	~70

track-etched membranes. For this purpose, polycarbonate foils (MAKROFOL N, Bayer) of thickness 30 μm were irradiated with swift heavy ions[5] and subsequently etched in aqueous 6 M NaOH at 50 °C. The pore diameter (and, hence, the wire diameter) was controlled by the etching time. The area density of the nanopores ranged from 10^7 to 10^8 cm^{-2}. After drying the etched foils, a gold layer was sputtered onto one side of the membrane which was reinforced by an electrochemically deposited copper layer. Thereafter, bismuth was deposited in the nanopores at 60 °C and −17 mV. Deposition was stopped as soon as caps were grown on top of the Bi needles. These caps were coated by another gold layer which served as a second electrode. The fabrication procedure has been discussed in more detail elsewhere [5], where it has been shown that under the employed conditions, we reliably produce wires of cylindrical shape which are strongly ⟨110⟩-textured and close to single-crystalline.

Obviously, this configuration is not suited for a real four point resistance measurement. However, by fixing thin Cu wires on the planar electrodes with silver conductive paint, distinct current and voltage contacts of ≈2 mm^2 were made on each side of the sample in order to realize a quasi four point measurement. Consequently, the measurement of contact resistances could not be avoided, but we could prove that they were very small, namely below 1 mΩ. Absolute resistance values of our samples are given in table 1. Also given are approximate numbers of wires in our samples. These are estimated in the following way: recent measurements of single bismuth nanowires, grown under exactly the same conditions as the wires investigated in the present work, revealed that at room temperature the resistivity of wires with diameters between 200 and 1000 nm was $\rho \simeq 315\ \mu\Omega$ cm—independent of the diameters [6]. Employing this result we find for the given geometries the number of wires in our samples as given in table 1.

Transport measurements were carried out in a ^{4}He cryostat reaching temperatures down to 1.5 K. The sample resistance was measured with a LR-700 resistance bridge, while the temperature control was implemented by a Lakeshore temperature controller and a carbon glass thermometer. The magnetic field of up to 6 T was oriented perpendicular to the long wire axis, so that in the temperature range from 1.5 to 50 K the transverse magnetoresistance was measured. In order to characterize our samples, we measured their resistances over the temperature range 1.5 K to room temperature (see figure 1). We observed the typical, non-monotonic behaviour with a resistance maximum shifting with changing diameter. Our overall results were in good agreement with recent measurements of single nanowires [6, 7] as well as of wire arrays [1, 2]. This indicates that the samples are of good quality and close to single-crystalline, as claimed above.

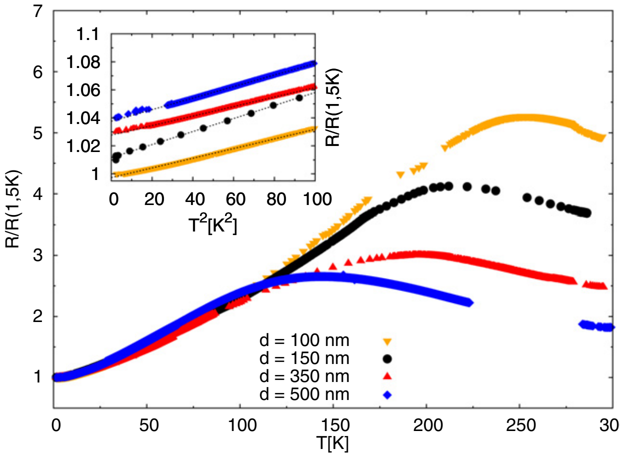

Figure 1. The main figure shows the temperature dependence of the resistance $R(T)$, normalized at $T = 1.5$ K, of arrays of nanowires with diameters d as indicated. The inset emphasizes the T^2 dependence of the resistivity at low temperatures. Here, curves are offset for clarity.

3. Results and discussion

3.1. Resistance at low temperatures

To emphasize the low temperature dependence we show our resistance data normalized to the value at $T = 1.5$ K. Unlike most other metals, the resistivity of bismuth was found to show a T^2 behaviour at low temperatures [8, 9]. This can be attributed to several different contributions. Already in 1937, Baber [10] predicted that collisions between electrons should contribute to the resistivity like $\rho_{\mathrm{e-e}} \propto (k_{\mathrm{B}}T/E_{\mathrm{F}})^2$, with k_{B} being the Boltzmann constant. For ordinary metals, this term is small as the Fermi energy is high. For bismuth, however, the Fermi energy is small ($E_{\mathrm{F}} \approx 25$ meV) [11], and the phonon scattering length is big, so that $\rho_{\mathrm{e-e}}$ becomes of considerable influence. Furthermore, carrier–carrier scattering resulting from the complex Fermi surface (as interband or electron–hole scattering) also results in T^2 terms in the resistivity [12, 13]. Finally, the anisotropic Fermi surface of bismuth causes even the phonon contribution to go as [14] $\rho_{\mathrm{e-ph}} \propto T^2$. Hence, the T^2 dependence should dominate the resistivity at low temperatures. This is clearly observed in our measurements for $T < 10$ K (see figure 1) and to our knowledge for the first time so clearly in Bi nanowires. It proves that crystal structure as well as band structure of our samples are intact. The good quantitative agreement of $R(T)/R(1.5\ \mathrm{K})$ up to about 100 K demonstrates that the temperature dependence of scattering processes and inelastic scattering lengths are very similar for all our samples independent of the wire diameter. They are much longer than the respective wire diameters as we discuss below.

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It is accepted [1, 2] that the reduction of the resistance at higher temperatures is caused by the rapid increase of carrier concentration. It is, however, less clear why this occurs at different temperatures for different wire diameters. As mentioned above we expect that, independent of the wire diameter, the resistivity of our electro-deposited Bi at 300 K is $\simeq$315 $\mu\Omega$ cm suggesting to plot the resistance data normalized at 300 K rather than 1.5 K. In such a plot the resistivity at low temperature appears to be the smaller, the thinner the wires are. Surprising at first glance, this behaviour may indeed be expected when on cooling the mean free paths ℓ of carriers become larger than the wire diameters d. In fact, mean free paths of 40 μm have been observed in single-crystalline nanowires with diameters of 240 nm [7]. Since the Fermi wavelength is large compared to atomic scale roughnesses, scattering from the surface is dominantly elastic and, in particular, thereby momentum conserving in transport direction. Usually, elastic scattering randomizes the momentum of the scattered carriers. The resulting wave guiding effects are more important the thinner the wires are and, assuming that ℓ becomes larger than d roughly at the resistance maximum we might argue that at low temperature the resistivity of a thin wire is indeed smaller than of a thick wire. Moreover, it was found that the texture of our electro-deposited Bi wires is the stronger the thinner the wires are [5, 6]. This would further strengthen wave guiding effects for thinner wires. The importance of specular surface scattering in cylindrical Bi wires (diameters between 0.2 and 0.8 μm) has been pointed out already by [15, 1] and more recently by [7]. We will come back to this point in our discussion of the magnetoresistance. The specular nature of the surface scattering may also explain why $R(T)$ of our wires exhibits such a clear T^2 dependence as expected for bulk material.

3.2. Magnetoresistance

We also investigated the magnetic field dependence of the sample resistance at various temperatures. Based on models applicable to semiconductors and compensated metals, the transverse magnetoresistance of bismuth is predicted to scale with B^2 for all field strengths, without saturation [16]. In contrast to this expectation, however, we found for all our samples an almost perfect $B^{1.5}$ dependence at temperatures between 1.5 and 50 K. This is demonstrated by the lines of figure 2. This clear deviation from the well-established theory raised the question whether theory was confirmed in older publications. Thorough examination of experimental literature on the magnetoresistance of bismuth showed that the B^2 law has hardly ever been confirmed, whereas power laws B^χ with $\chi \neq 2$ often describe the data very well. In [17] for example, where single-crystalline bulk bismuth is investigated, a $B^{1.66}$ dependence is obtained by a best fit, but no physical explanation is suggested. Furthermore, an analysis of the data in [18] revealed a clear $B^{1.33}$ dependence for the magnetoresistance of the measured polycrystalline bismuth nanowires. Other publications on Bi nanowires [1, 4, 19] either do not mention the B^2 dependence or only try to confirm it for limited magnetic field ranges.

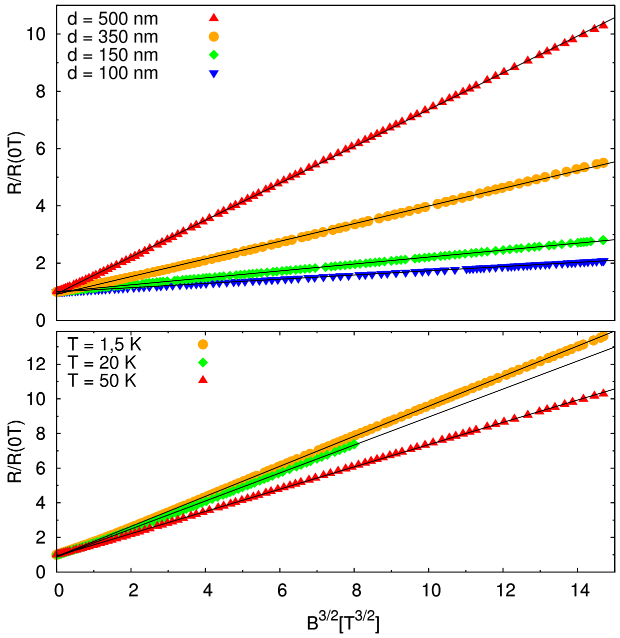

Figure 2. Magnetoresistance of our Bi samples plotted versus $B^{3/2}$. The upper panel shows the behaviour of wires with various diameters at $T = 50$ K. The lower panel shows the behaviour of wires with a diameter of 500 nm at different temperatures as indicated.

After all, a magnetic field dependence of the magnetoresistance having the form B^χ, with exponents varying from $\chi = 1.33$ to 1.66, seems to be a well-established experimental fact. Close inspection of our own data reveals that χ is slightly larger than 1.5 for fields up to 2 T and a little smaller than 1.5 for higher fields. Obviously, the theory predicting the B^2 dependence is based on a model that is too simple to account for the complex band structure of bismuth.

Two more points are to be noted in the context of figure 2. Firstly, the magnetoresistance depends strongly on the diameter of the Bi wires. Extracting slopes from the upper panel, we find the relative variation of the resistance $(R(B) - R(0\ \mathrm{T}))/R(0\ \mathrm{T})$ to follow nicely a d^2 dependence. We have discussed above that the band structure of our Bi wires seems not to depend on their diameter. We may argue, however, that along with specular reflections becoming more important the transport in thinner wires is less sensitive to magnetic fields. Carriers having trajectories with small incident angle are dominant and their skipping orbits in a magnetic field will have only a small undulation. Secondly, the measured magnetoresistance decreases slowly with temperature T (see lower panel of figure 2). For all of our samples, this is well described by a linear dependence $-\alpha(B)T$ between $T = 1.5$ and 50 K. Additionally, the absolute value of this slope was found to grow as B is increased (data not shown).

In combination with the T^2 dependence of the resistance discussed above, this second effect gives rise to a surprising and interesting anomaly shown in figure 3. At finite magnetic fields B, the resistance varies in a parabolic curve shape with a minimum at a certain temperature $T_{\mathrm{min}} \neq 0$. For a given sample, this minimum was shifted to higher temperatures as the magnetic field was increased. This behaviour was entirely

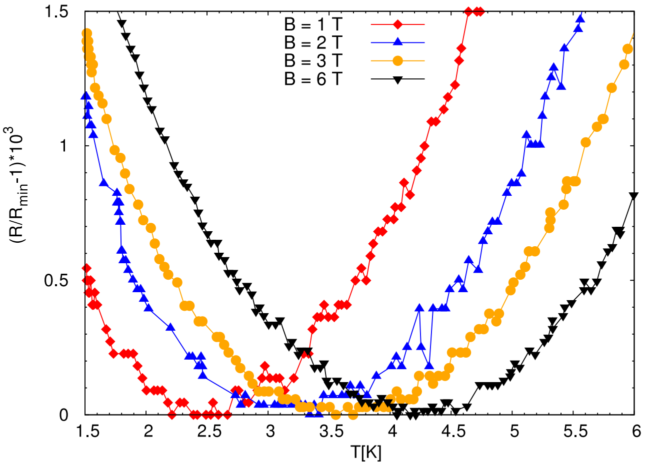

Figure 3. Normalized resistance versus temperature for our sample with wire diameter $d = 150$ nm. An applied magnetic field B led to a resistance minimum at $T = T_{\mathrm{min}}$. With growing B, the minimum was shifted to higher temperatures.

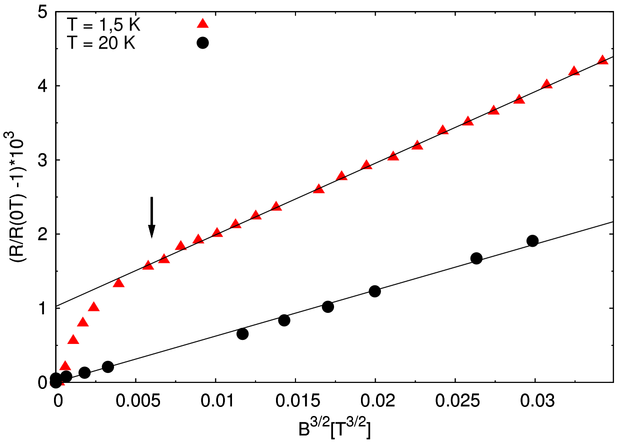

Figure 4. Steplike increase of the magnetoresistance of our sample with $d = 100$ nm. The arrow indicates the critical magnetic field $B_{\mathrm{c}} = 33$ mT. The dashed lines point out the normal $B^{1.5}$ dependence. The slopes for 1.5 and 20 K are different because of the temperature dependence of the magnetoresistance, as explained above.

unexpected and could neither be found in experimental nor in theoretical literature. Combining the temperature dependence at zero field, $\rho_{B=0} \propto T^2$ with the magnetic field effects discussed above we find a new phenomenological function for the resistivity, namely $\rho = \delta T^2 - \alpha(B)T + \beta(B)$. Here, both the offset β and the linear coefficient α are increasing with magnetic field. Consequently, the parabolic dependence should be preserved for $B \neq 0$, and a resistance minimum should be obtained at $T_{\mathrm{min}} = \alpha/(2\delta)$, moving to higher temperatures as B (and hence α) is increased. Both effects can clearly be observed in figure 3.

Although our observations present a rather clear and consistent picture an unambiguous interpretation is not possible at present. Partially, this is owed to some apparent discrepancies with other experiments [1], where for wires with 70 nm diameter a decreasing magnetoresistance with temperature was reported (as in our experiments), for wires with 200 nm diameter, however, an increasing magnetoresistance was found. Those results were obtained from a B^2 fit in the field range $0\ \mathrm{T} < B < 1\ \mathrm{T}$. Moreover, the crystalline orientation in transport direction was different from ours. To learn more about the observed effects it seems to be necessary to investigate different orientations of the magnetic field with respect to the wire axis and of the crystalline direction the wires are grown along. Again, a satisfying and reliable explanation of the temperature dependence of the magnetoresistance may only be reached by a detailed consideration of the complex and highly anisotropic Fermi surface of bismuth.

3.3. Localization effect

Finally, in figure 4, we show the magnetoresistance of our thinnest wires at two different temperatures. At 1.5 K, additionally to the $B^{1.5}$ dependence discussed above, a distinctly steeper increase is observed at very small field strengths which is not present at 20 K. Similar effects have been observed recently by Heremans *et al* [4] for the transverse and longitudinal magnetoresistance of arrays of Bi wires with diameters up to 48 nm. The effect has been interpreted in terms of localization where the influence of a magnetic field is expressed by a characteristic length scale $l_B = \sqrt{\hbar/(2eB)}$. For thin wires, a critical magnetic field B_{c}, where the wire diameter equals the magnetic length ($l_B(B_{\mathrm{c}}) = d$), can be defined. While for $B < B_{\mathrm{c}}$ the electronic wavefunctions are confined by the wire diameter, they are confined by the magnetic field for $B > B_{\mathrm{c}}$. Consequently, a cross-over from one- to three-dimensional behaviour can be expected. For $d = 100$ nm, $B_{\mathrm{c}} = 33$ mT. As indicated by the arrow in figure 4, this is just where the steeper increase bends over to the normal $B^{1.5}$ dependence. Although this result confirms and extends the earlier experiments [4] we are not fully convinced by the given interpretation. After all, localization phenomena are based on multiple scattering processes and thus require sufficient disorder. This is probably not the case in our samples given the long mean free paths, which quite likely exceed 10 μm at low temperatures. On the other hand, the reduced dimensionality would certainly enhance any localization effects. Future experiments might clarify this question.

4. Conclusions

In conclusion, we have observed a novel effect on bismuth nanowire arrays. In the presence of a magnetic field, the temperature dependence of their resistances had a parabolic shape with a minimum at a temperature $T_{\mathrm{min}} \neq 0$, shifting to higher temperature as B is increased. This effect could be related to the temperature dependence of the magnetoresistance. Furthermore, a clear $B^{1.5}$ dependence of the magnetoresistance was found, which agrees well with older experiments but not with theory. In addition, a steplike increase of the magnetoresistance was observed on our sample with wire diameter of 100 nm, extending the results of Heremans *et al* to larger diameters. This effect was attributed to the transition from one- to three-dimensional localization. $R(T)$ measurements suggest that surface scattering in our Bi nanowires is specular allowing e.g. the observation of a clear T^2 dependence below 10 K.

Acknowledgments

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