PHYSICAL REVIEW B

CONDENSED MATTER AND MATERIALS PHYSICS

THIRD SERIES, VOLUME 58, NUMBER 16 15 OCTOBER 1998-II

RAPID COMMUNICATIONS

Rapid Communications are intended for the accelerated publication of important new results and are therefore given priority treatment both in the editorial office and in production. A Rapid Communication in **Physical Review B** *may be no longer than four printed pages and must be accompanied by an abstract. Page proofs are sent to authors.*

Magnetoresistance of bismuth nanowire arrays: A possible transition from one-dimensional to three-dimensional localization

J. Heremans and C. M. Thrush
General Motors Research and Development Center, Warren, Michigan 48090-9055

Z. Zhang and X. Sun
Department of Physics, Massachusetts Institute of Technology, Cambridge, Massachusetts 01239-4307

M. S. Dresselhaus
Department of Electrical Engineering and Computer Science and Department of Physics, Massachusetts Institute of Technology, Cambridge, Massachusetts 01239-4307

J. Y. Ying
Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 01239-4307

D. T. Morelli
General Motors Research and Development Center, Warren, Michigan 48090-9055

(Received 25 June 1998)

This paper reports a series of magnetoresistance measurements made on arrays of bismuth nanowires with diameters ranging from 28 ± 3 to 70 ± 10 nm. The data were taken between 1.4 and 10 K in magnetic fields from 0 to 5 T. The magnetoresistance curves below 4.2 K show a steplike increase in magnetoresistance relative to the curves at 4.2 K, occurring at the field at which the magnetic length L_H equals the wire diameter d. At low B fields where $L_H > d$, the electron wave function is confined by the wire diameter, while at high magnetic fields for which $L_H < d$, the carriers are in a bulklike environment. These results suggest that the steplike magnetoresistance is due to a transition between one-dimensional (1D) localization and 3D localization. [S0163-1829(98)51240-4]

The electronic transport properties of thin wires in the temperature and field regime where localization effects are dominant have been the object of many studies over the last two decades. Localization effects[1,2] and resistance fluctuations[3] have been studied extensively in films and wires of polycrystalline bismuth. The semimetal Bi is often selected for such studies because the electron density is some five orders of magnitude smaller than in conventional metals. The resistivity of Bi is, therefore, large in spite of the extremely large electron mean free path, and this in turn enhances the importance of resistance anomalies. Furthermore the very small effective mass of electrons in Bi results in a large spatial extension of the electron wave functions; the effects of reduced dimensionality can therefore be seen in samples with dimensions on the order of 100 nm. Quantization of the conductance in Bi nanocontacts formed between two Bi electrodes has been observed.[4,5] Classical electron transport in single-crystal Bi wires of diameters below 200 nm have also shown one-dimensional-like (1D) behavior in both Shubnikov–de Haas (SdH) oscillations and in the temperature and magnetic-field dependence of the resistivity.[6–8] The influence of the dimensionality on the contribution of localization effects to the magnetoresistance has been the subject of considerable theoretical work, reviewed in Ref. 9. In this work, we present experimental data on the magnetoresistance of a new class of samples that consists of an aligned parallel array of single-crystal Bi wires, 28 to 70 nm in diameter, imbedded in an anodic alumina template, in the tem-

perature range in which localization phenomena are known to become important. We observe an increase in magnetoresistance below 4 K which occurs at a characteristic magnetic-field value that depends only on the diameter of the wire and not on the direction of the field with respect to the wire axis or the temperature, provided that $T<4$ K. Since the band structure of Bi is highly anisotropic, this characteristic field is not related to the effective mass of the carriers. The characteristic field corresponds to the value at which the magnetic length equals the wire diameter, and the observed effect is attributed to a transition from 1D localization at low field to 3D localization at high field. This work complements that of Ref. 1, in that Beutler and Giordano[1] deliberately remained at low magnetic fields in order to study the localization in 1D quantitatively, while here the field is swept to cover the 1D to 3D transition. Furthermore, the wires studied here are single crystals, while in Ref. 1 the grain size of the samples was deliberately kept in the 10–20-nm range.

We prepared five arrays of Bi nanowires for this study, four of which show localization effects. The host material is insulating amorphous Al_2O_3, prepared by anodic oxidation of Al.[10] The fifth sample contained wires of 200 nm diam, prepared from commercially available Whatman Anodisc alumina. The host material of all five samples consists of a flat alumina plate, about 50 μm thick, that has an array of pores running parallel to each other throughout the thickness of the plate. A plan-view scanning electron microscopy (SEM) image of one sample of porous Al_2O_3 host material with 28 nm pores is shown in Fig. 1(a). The pore diameters, as well as the average distance between pores, are determined from SEM studies and are given in Table I. The pores were filled with Bi metal using a vacuum evaporation technique that will be described in a separate paper and is different from the high-pressure liquid injection technique used both in recent[10] and earlier[6–8] work. An edge-view SEM image of the Bi wires running through the host material is shown in Fig. 1(b). As it is possible to dissolve the Al_2O_3 by a selective etch that does not attack the Bi wires, transmission electron microscope samples have been prepared consisting of free-standing Bi wires, and lattice fringe images show that individual wires are single crystals throughout their length. The wire diameter was uniform to within 10% over the length of the wires in samples Bi*J*1–Bi*J*4, and to within 25% on wire Bi*J*5. X-ray diffraction (XRD) patterns show that over 90% of the wires are oriented along the [0, 0.949, 0.315] direction in the rhombohedral $[x,y,z]$ system.[11] Semimetallic samples with diameters of 200–70 nm do show SdH oscillations. Since these are not simply periodic in $1/B$,[6] their in-depth study is deferred to a subsequent paper.

The two-probe resistance of each array of wires connected in parallel to each other was measured by making contacts to the top and bottom faces of the anodic alumina plate. Silver epoxy and silver paint were used as contact materials. The contact areas were on the order of a fraction of a mm^2 on each side. The two-probe resistance of the arrays was on the order of several hundred Ω to several kΩ. It can be seen in Fig. 1(b) that Bi metal extends out of the pores on both sides of the alumina plate, and the silver paint makes contact to those metallic extensions; it is therefore believed that the contact resistance, which is typically of the order of a fraction of an Ω between silver paint and bulk Bi, is small compared to the sample resistance. The resistance was measured using a self-balancing low-frequency ac bridge (linear instruments LR-700) with excitation voltages that were varied from 20 μV to 2 mV. The excitation voltage level did not affect the results; most traces were recorded at either 200 or 600 μV. The data reported here were taken on one sample each of wire arrays Bi*J*4 (Bi*J*4*A*) and Bi*J*5, and on two samples of wire arrays Bi*J*1 (Bi*J*1*A* and Bi*J*1*B*) and Bi*J*2. The sample-to-sample repeatability was excellent. Figure 1(b) shows that only a fraction of the wires extend all the way through the sample. Since it is impossible to estimate this fraction, unfortunately, the actual resistance value of each wire is unknown.

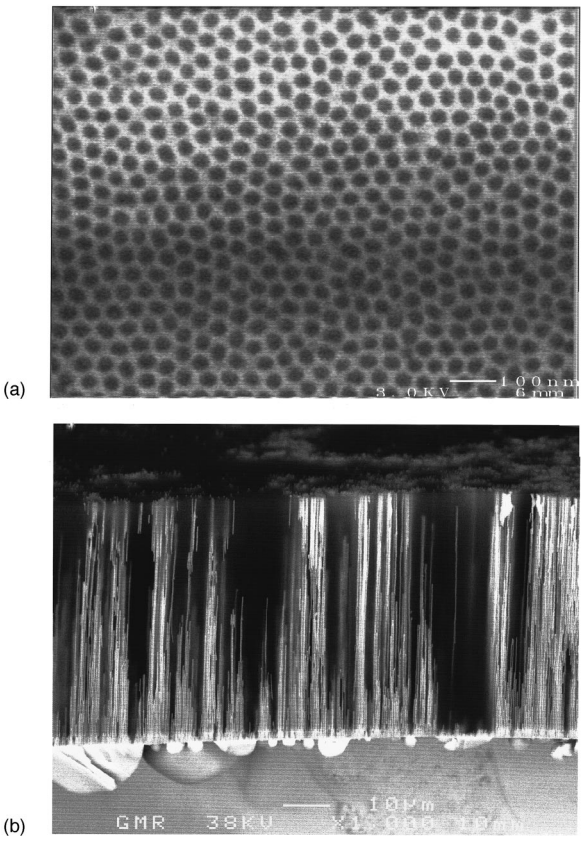

FIG. 1. (a) Plan-view SEM image of an Al_2O_3 template, here with 28 nm pores; (b) edge-view SEM image of an Al_2O_3 template (dark) filled with Bi wires (bright), here with 200 nm pores.

From the quasiclassical effective-mass model of pure Bi, it can be calculated that a semimetal-to-semiconductor transition takes place as the wire diameter is reduced from below

TABLE I. Dimensions of the pores in the alumina templates that were used, and residual resistance ratio of the Bi wires.

Sample	Average wire diameter (nm)	Average spacing between wires (nm)	$\frac{R\ (300\ \mathrm{K})}{R\ (4\ \mathrm{K})}$
Bi*J*1	70±10	160	1.12
Bi*J*2	36±5	75	0.53
Bi*J*4	48±6	116±6	0.46
Bi*J*5	28±3	45±4	0.63
Bi*W*9 and Bi*W*11	200	400	0.97

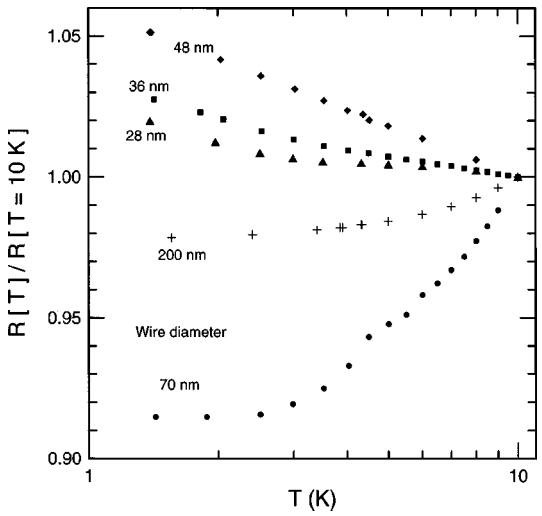

FIG. 2. Temperature dependence of the zero-field resistance of Bi nanowires of different diameter, normalized to the resistance at 10 K.

100 to 28 nm. As a result, the temperature dependence above 4 K of the resistance and magnetoresistance of Bi nanowires is complicated by the fact that both the electron density and mobility are temperature and size dependent.[8,11] The residual resistance ratio $[R(300\ \mathrm{K})/R(4\ \mathrm{K})]$ is given in Table I. The present report is focused on the temperature regime ($T<5$ K) where localization effects are observed.

Figure 2 shows the temperature dependence of the zero-field resistance $R(T)$ of the samples studied. The data are presented normalized to 10 K, and denoted by $R(T)/R(T=10\ \mathrm{K})$. As discussed in Ref. 1, the temperature coefficient of the contribution of localization effects to the resistance can be positive or negative, depending on the wire diameter. Furthermore, the semimetal-to-semiconductor transition mentioned above, and the nonnegligible contribution of acoustic-phonon scattering in the wider single-crystal wires (as opposed to the fine-grain polycrystalline wires studied in Ref. 1) all complicate the analysis of the temperature dependence of the resistance. Again, this report is focused on the diameter regime ($d\leqslant 50$ nm), where localization effects are most visible.

Figure 3 shows the relative longitudinal magnetoresistance as a function of magnetic field of the four wire arrays with diameters smaller than 200 nm at a few different temperatures; the magnetic field is applied parallel to the current and to the wires' longitudinal axis. SdH oscillations are visible for sample Bi*J1A* above 2 T. Figure 4 shows the transverse magnetoresistance (MR), with the magnetic field applied in a direction normal to the current. In both figures, the resistance $R(B)$ is normalized to its value at zero magnetic field, $R(B=0\ \mathrm{T})$.

The longitudinal and transverse magnetoresistance curves at 1.4 K show a resistance increase over the curves at 4.2 K. In the narrower wires ($d=28$, 36, and 48 nm in the longitudinal MR, and 28 and 36 nm in the transverse MR), the difference curve between the two, which the readers can easily visualize, is a rounded step function starting at 0 T and saturating at a field value that depends on the diameter of the wire, but not on temperature. Hints of a similar contribution begin to appear in the 70-nm wire in longitudinal configuration, and in the 48-nm wire transverse direction, while no effect is observed in the transverse MR on the 70-nm sample, or in any direction in the 200-nm wires (not shown).

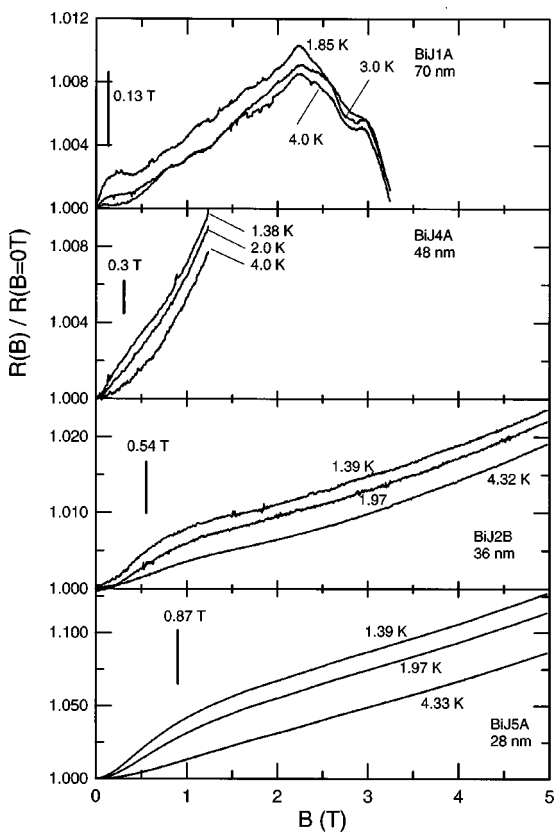

FIG. 3. Longitudinal magnetoresistance as a function of magnetic field, normalized to the resistance at zero field, for Bi nanowires of the diameters indicated. The vertical bars indicate, for each sample, the magnetic field B_c at which the magnetic length equals the wire diameter.

Very schematically, several length scales are relevant to localization problems: the wire diameter d, the phase-breaking length L_ϕ, and the magnetic length L_H, which corresponds to the spatial extent of the wave function of the electrons in the lowest Landau level:

$$L_H=(\hbar/eB)^{1/2}. \tag{1}$$

Vertical lines in Figs. 3 and 4 represent, for each sample, the value of the critical magnetic field B_c where the condition

$$L_H(B_c)=d \tag{2}$$

is satisfied. At fields above B_c, the Landau orbit size is smaller than the wire diameter, and the conductivity is essentially three dimensional. At fields below B_c, the electron wave function is more confined by the wire walls than by the magnetic field, and the transport is more one dimensional. It is clearly observed in Figs. 3 and 4 that the value B_c corresponds rather well to the characteristic field at which the 1.4-K magnetoresistance shows a steplike increase over the 4-K magnetoresistance. The observed location of the increase in magnetoresistance is temperature independent, as is B_c. The increased magnetoresistance occurs at the same field for both field orientations, and this is consistent with condition [Eq. (2)], which is independent of the effective

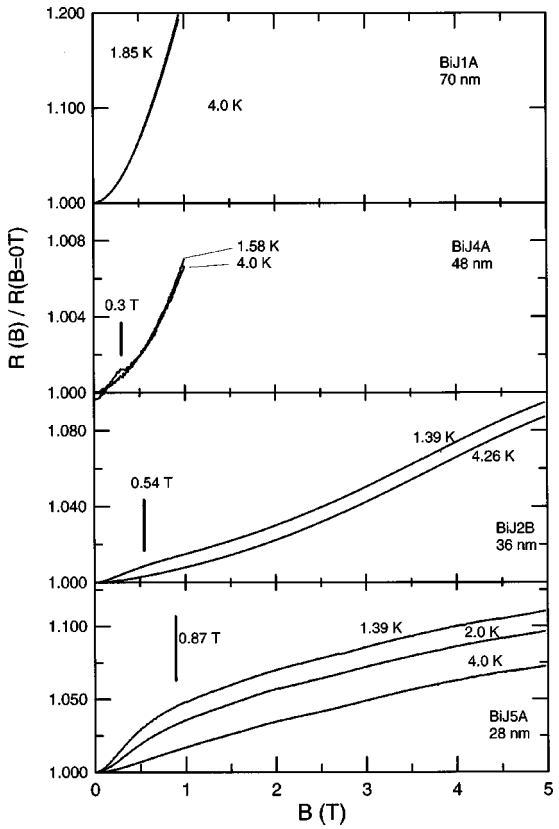

FIG. 4. Transverse magnetoresistance as a function of magnetic field, normalized to the resistance at zero field, for Bi nanowires of the diameters indicated. The vertical bars indicate the magnetic field B_c at which the magnetic length equals the wire diameter.

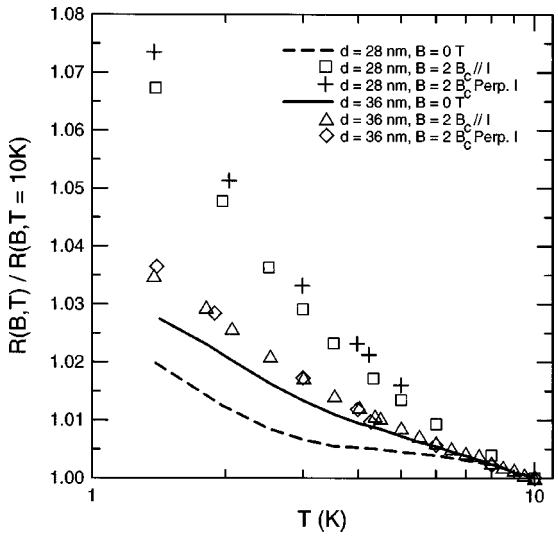

FIG. 5. The temperature dependence of the resistance of the 28- and 36-nm Bi nanowires, normalized to 10 K, at zero magnetic field (lines) and at magnetic-field values equal to twice the critical field B_c (at $B=1.74$ T for the 28-nm wire and at $B=1.08$ T for the 36-nm wires).

mass, a very anisotropic quantity in Bi. All these observations, together with the relation between the excess magnetoresistance and the magnetic flux quantum via the quantity L_H, leads us to attribute the observed increase in magnetoresistance to carrier localization. This is a one-dimensional effect as long as both the phase-breaking length L_ϕ and L_H are larger than d, and a 3D effect otherwise. Since in the single-crystal wires studied here, mechanisms other than localization probably contribute to the temperature dependence of the resistance, it is not possible to deduce L_ϕ directly from the data. In polycrystalline Bi,[1] it is found that $L_\phi \propto T^{-p/2}$ with $p=1.45\pm0.10$, and furthermore L_ϕ at 1.4 K is on the order of 50 to 63 nm for polycrystalline wires with diameters of 36.5 and 52.5 nm, respectively. It is likely that L_ϕ is larger for the single-crystal wires studied here. Since, furthermore, the observed transition occurs at a temperature-independent field for $T \leqslant 2$ K, the condition $L_\phi > d$ is probably satisfied below roughly 2 K for all samples but Bi*J1A*. It is therefore probable that the observation of an added magnetoresistance at $B > B_c$ ($L_H = d$) is due to a transition from 1D to 3D localization. The field dependence of the effect is smeared out, in part because of the wire diameter distribution inside each sample, due to both wire-to-wire variations and to longitudinal nonuniformities.

While the value of B_c is not a function of temperature, the amplitude of the excess magnetoresistance is. Figure 5 shows the resistance $R(B,T)$, normalized to the value at 10 K, $R(B,T=10\text{ K})$, of the two narrowest wires at zero field (these data are repeated from Fig. 2) and at a field value equal to twice B_c, where the excess magnetoresistance is almost saturated. The resistances have the same temperature dependence in both transverse fields and longitudinal fields, but the temperature dependence at $B=2B_c$ is quite different from that at $B=0$ T. Both here and in Ref. 1, the localization effects appear in the same temperature range ($T<4$ to 5 K), which implies that the temperature-dependent part of L_ϕ is rather similar. Inelastic scattering, which below 5 K is dominated by electron-electron interactions, plays a key role in localization effects in polycrystalline Bi wires[1] and therefore probably in this work as well. Unfortunately, because the conductivity of a single wire is unknown in the present setup, the scattering time cannot be determined quantitatively. As the primary purpose of this paper is to present new experimental data, no further attempt at a quantitative analysis of the temperature and field dependence of the resistance has been made.

In summary, magnetoresistance measurements on four arrays of single-crystal Bi nanowires with diameters below 70 nm show a smeared steplike increase in the magnetoresistance at magnetic fields above the value at which the magnetic length becomes smaller than the wire diameter. The field at which this additional magnetoresistance appears is temperature independent and isotropic, which is consistent with the fact that the magnetic length does not depend on the band structure of the solid. The additional magnetoresistance is therefore ascribed to a transition from 1D localization at low field to 3D localization at high field, where the electron wave functions extend over a distance smaller than the wire diameter.

The authors acknowledge helpful discussions with Dr. G. Dresselhaus. The MIT authors received support from the National Science Foundation through Grant Nos. CTS-9257223 and DMR-9400334, and the US Navy through Contract No. N00167-92-K0052, and MURI subcontract with UCLA Contract No. 0205-G-7A114-01.

[1] D. E. Beutler and N. Giordano, Phys. Rev. B **38**, 8 (1988).
[2] P. H. Woerlee *et al.*, J. Phys. C **16**, 3011 (1983).
[3] D. E. Beutler *et al.*, Phys. Rev. Lett. **58**, 1240 (1987).
[4] J. L. Costa-Krämer *et al.*, Phys. Rev. Lett. **78**, 4990 (1997).
[5] N. Garcia *et al.*, in *Nanowires*, edited by P. A. Serena and N. Garcia (Kluwer Academic, The Netherlands, 1997), pp. 243–250.
[6] N. B. Brandt *et al.*, Zh. Eksp. Teor. Fiz. **92**, 913 (1987) [Sov. Phys. JETP **65**, 515 (1987)].
[7] N. B. Brandt *et al.*, Zh. Eksp. Teor. Fiz. **72**, 1226 (1977) [Sov. Phys. JETP **45**, 1226 (1977)].
[8] M. Gurvitch, J. Low Temp. Phys. **38**, 777 (1980).
[9] P. A. Lee and T. V. Ramakrishnan, Rev. Mod. Phys. **57**, 287 (1985); G. Bergmann, Phys. Rep. **107**, 1 (1984).
[10] Z. Zhang *et al.*, J. Mater. Res. **13**, 1745 (1998).
[11] The Bi nanowires in this study have an XRD pattern very similar to that of the nanowires grown by high-pressure liquid injection described in Z. Zhang, X. Sun, M. S. Dresselhaus, J. Y. Ying, and J. Heremans, Appl. Phys. Lett. **73**, 1589 (1998). This reference also contains a study of the resistance and magnetoresistance at temperatures above 4 K, where localization effects are negligible. For the purpose of the present study, this reference shows that Bi wires with diameters $d \leqslant 50$ nm may be viewed as a degenerately doped semiconductor.