Conductance Quantization in Bismuth Nanowires at 4 K

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(Received 7 November 1996)

Conductance experiments on Bi nanowires at 4 K, obtained with a scanning tunneling microscope, are presented. The conductance of these Bi nanocontacts, formed between two Bi electrodes, exhibits plateaus at quantized values of $G_0 = 2e^2/h$, remaining basically constant during electrode separations of about 50 nm. This is the first time that such plateaus have been observed in semimetals. The histogram of conductance values, constructed with thousands of consecutive contact breakage conductance experiments, exhibits clear peaks at G_0 and $2G_0$. [S0031-9007(97)03366-8]

PACS numbers: 73.20.Dx, 73.23.Ps

Conductance quantization (CQ) in metallic nanowires at room temperature (RT) has been experimentally achieved recently; fabricating these nanocontacts by bringing together and separating two metallic electrodes. These experiments have been performed using scanning tunneling microscopy (STM) techniques [1,2], by simply getting two macroscopic wires in and out of contact with tabletop experiments [3], and using the mechanically controllable break junction (MCBJ) technique [4]. The observed conductance plateaus (at about $G_0 = 2e^2/h$, where e and h are the electrons charge and Planck's constant, respectively) last between 0.05 and 0.4 nm electrode separations [5], for metals like Au, Ag, Cu, Na, etc., of the order of the Fermi wavelength ($\lambda_F = 0.5$ nm) or the atom size in these metals. The same results are observed for gold nanowires at 4 K, and up to seven quantum conductance peaks are well resolved in the conductance histogram [5]. In order to clarify the current understanding of the phenomenon of CQ, measurements in semimetals are very attractive. Previous experiments in antimony have failed to observe CQ plateaus using the MCBJ technique at low temperature [4]. Furthermore, the existence of subquantum conductance plateaus was interpreted [4] as evidence of a conductance determined by atomic rearrangements, but no conductance histogram was presented. While CQ can be observed at RT for metals with Fermi energies of 6 eV, for semimetals this value is tens of meV ($\lambda_F \sim 10$–30 nm), and CQ can be observed only at low temperatures, like in GaAs devices [6].

In this Letter we present the first experimental evidence of CQ in Bi at 4 K, exhibiting conductance plateaus that last about 20–100 nm electrodes separation, demonstrating that quantization may not be due to atomic rearrangements but to the existence of well defined quantum states localized at the constriction formed between two Bi electrodes: $E_F \sim 25$ meV and carrier concentration $\sim 4 \times 10^{17}\ e/\mathrm{cm}^3$ [7,8]. This leads within the parabolic effective mass approximation to $\lambda_F \sim 26$ nm and an effective mass of $\sim 0.07 m_0$, where m_0 is the electron rest mass. In addition, we present conductance histograms with no sample selection showing peaks at integer values of G_0, and, current-voltage characteristics (I-V curves) that exhibit quantum breaks in the conductance at certain voltage values. These I-V curves are quite different than those observed for metals [5].

The experiments are performed in a homemade low temperature STM. This unit is placed inside a dipstick, working at a low He gas pressure environment. The dipstick is evacuated and filled with He gas several times before placing it inside the liquid helium bath. Two freshly cleaved pieces of high purity (99.99%) polycrystalline Bi electrodes are placed in the tip and sample positions, from now on referred to as the "tip" and the "sample." The tip is mounted in a quartered piezotube that allows movement in the vertical (Z, up to 1.4 μm with 280 V) and horizontal X-Y, up to 8 μm with 280 V) directions. A low potential difference is applied to the sample, typically few tens of mV. While the sample is fixed, the tip is driven in and out of contact with the sample, feeding a triangular wave to the piezoelectric Z electrodes. The electrodes' approach-separation speed can be modified by changing the amplitude and/or frequency of this signal. The current is measured with a current-voltage (I-V) converter, working at 10^5 gain (100 mV/μA), with 1 μs risetime and 3 μs settling time. The excursions in and out of contact result in current excursions from the saturation value of the I-V converter (about 12 V corresponding to 120 μA) to zero. The current signal is measured with a LeCroy 9354AM digital oscilloscope, with 500 MHz bandwidth and 2×10^9/s sampling rate. The data acquisition is triggered properly to build, in real time, conductance histograms with all the measured conductance curves which correspond to consecutive contact breakage current decays. The raw histogram can be filtered slightly or corrected in order to avoid problems due to the nonideal differential linearity (NIDL) of the digital oscilloscope [5,9]. Figure 1 shows a schematic drawing of this experimental procedure.

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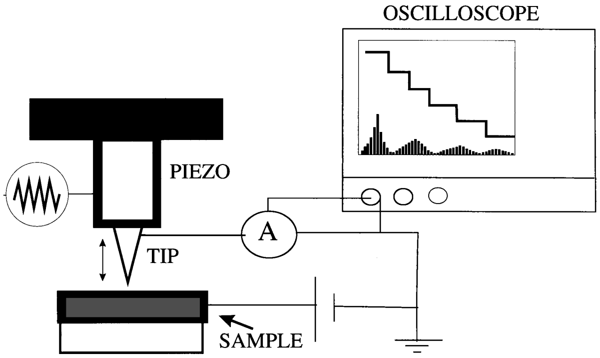

FIG. 1. Schematic drawing of the experimental setup used to measure the conductance of Bi nanowires at 4 K. The STM unit is placed inside a dipstick working under a low pressure of He gas. A Bi tip is crushed repeatedly onto a Bi surface, driving the tip piezo with a triangular signal. The conductance is measured at the last stages of the contact breakage process. The conductance histogram is built with all the measured curves and is displayed in real time.

In Figs. 2(a)–2(c) we display selected current decays (conductance in the vertical right axis) during the Bi tip retraction at 4 K. The tip separation speed is 17 μm/s. The lower horizontal axis shows the time lapsed from the trigger point, and the upper one displays this time multiplied by the electrode speed, i.e., the separation distance between electrodes measured from the trigger point. The data present remarkable conductance plateaus at about G_0 and $2G_0$ ($G_0 = 2e^2/h \sim 77.5\ \mu\text{S} \sim 1/12\,907\ \Omega$). Notice the steps duration. In the case of metals, the length of these plateaus is typically between 0.05 and 0.4 nm (the Fermi wavelength, λ_F, is about 0.5 nm) under the same experimental conditions [1–3,5,9]. As shown in Fig. 2, for Bi these steps durations range between 20 and 100 nm, also of the order of the electron λ_F in Bi, about 26 nm. The conductance plateaus can be explained in terms of the cross section change needed in order to introduce or remove electronic quantum levels in the constriction. This cross section change should be of the order of λ_F, requiring elongations of that order of magnitude. It should be mentioned that this kind of evolution, in which long conductance steps are present, is not always observed when breaking the contact between Bi electrodes. However, when the conductance starts exhibiting this clear stepped behavior, it does it quite reproducibly, with the conductance plateaus quite close to integer values of G_0, as demonstrated by the histogram shown below. Disorder can account for the deviations of the measured conductance from integer multiples of $2e^2/h$ [10] that correspond to a perfectly ordered nanowire. It is also possible that, due to the larger number of atoms involved in the contact, these semimetals nanocontacts are more sensible to disorder [10] than their metallic counterparts. In this view, the shape of the contact and the detailed atomic configurations will be much more critical parameters in order to observe CQ. Nevertheless, some of the observed plateaus are perfectly horizontal like the ones shown in Figs. 2(b) and 2(c).

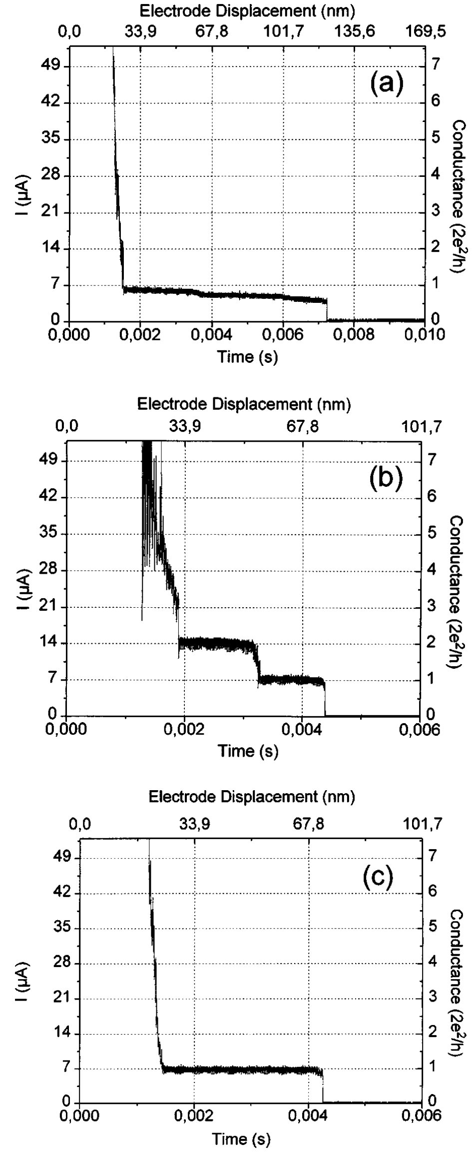

FIG. 2. (a)–(c) Conductance decay curves when a Bi tip crushes into and separates from a Bi surface at 17 μm/s, with an applied bias of 90.4 mV. The upper horizontal axis displays the corresponding electrode separation (time lapsed from the trigger point multiplied by electrode speed). Notice the large conductance step durations, 20–100 nm.

It has been suggested [4,11] that quantized conductance is simply a consequence of atomic rearrangements, because subquantum conductance plateaus are observed for antimony [4], and force jumps occur simultaneously with conductance jumps in gold at RT [11]. The nanowire deformation mechanism [12] has to be considered, but, while it is clear that the atoms in the contact have to rearrange in order to change the contact cross section, that does not necessarily imply that this cross section changes abruptly, especially from the electrons' point of view since they move much faster than atoms. The measured force jumps are attributed in [11] to abrupt atomic rearrangements (abrupt section changes), although this hypothesis has not been verified. The force jumps might be very well due to the conductance jumps themselves, due to squared root singularities of the density of states every time that a new mode enters or exits the constriction [13], and the abrupt atomic rearrangements have not been observed. The experiments presented here were carried out to check the hypothesis that conductance jumps occur only when there are abrupt atomic rearrangements. The data presented here suggest that under certain conditions this is not the case, because it is difficult to imagine that there are no atomic rearrangements when the tip is pulled 20–100 nm. Remember that for Au the force jumps where observed at intervals of ~0.2 nm [11].

Figure 3 displays conductance histograms built with 1736 and 3004 consecutive conductance curves. The raw data are corrected for the nonideal differential linearity of the oscilloscope [9]. As observed, there are two clear conductance peaks at about G_0 and $2G_0$, and some structure at about $3G_0$ and $4G_0$. Although the statistics average out some information, these histograms are experimental evidence of a large number of curves with plateaus at integer values of the quantum of conductance, G_0. In addition, we have performed the same experiment at room temperature, and the conductance histograms, built with a few thousand curves, are flat.

The current dependence on the bias voltage (I-V characteristic) can be measured during a contact breakage. In this experiment, the tip is retracted very slowly while sweeping the bias fast, in such a way that during one bias cycle the nanowire is quite close to a static situation. Three selected I-V curves during one contact breakage are displayed in Fig. 4. The observed I-V curves are quite different than those for metallic nanocontacts like Au [5] under the same conditions. A linear dependence plus a smooth varying nonlinear part is found for gold at RT [5]. On the otherhand, Bi exhibits rather smooth slope transitions at low conductance values, as shown in Fig. 4. Two I-V curves at high ($\sim 10G_0$ and $19G_0$) conducting channels are shown, demonstrating a good linearity n the applied bias range. After further retracting the tip a position is reached where the conductance is zero at low bias; however, on increasing the voltage (part A in the graph) the conductance suddenly increases again (B). When the bias decreases (C) the conductance goes again to zero, with marked slope transitions. Notice also a similar behavior in the positive part of the I-V curves denoted by D-E-F-G. We believe that this anomalous behavior might be due to the addition or removal of conducting channels due to the applied bias. Working at hundreds of mV bias, several times the Fermi energy, the electron energy in the nanocontact could not be the Fermi energy anymore. This energy would be provided by the huge electric field at the constriction. On increasing or decreasing the bias, the electron energy and its wavelength would be modified, and depending on the size of the nanowire, the number of modes that can contribute to the transport.

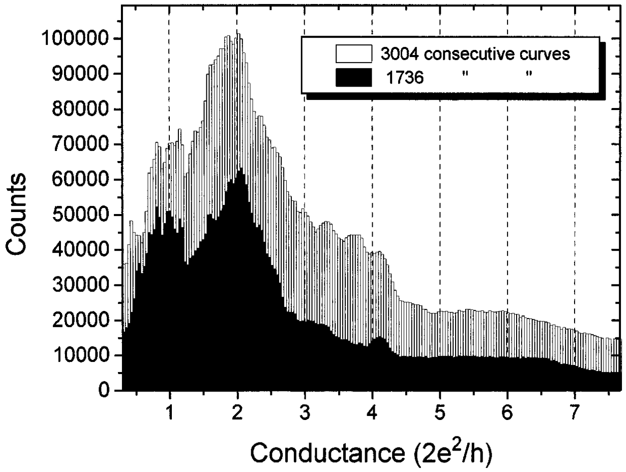

FIG. 3. Conductance histogram for Bi nanowires at 4 K built with 1736 and 3004 consecutive curves. The applied bias between tip and sample is 90.4 mV; the tip speed is 1.4 μm/s. The raw data are corrected for the nonideal differential linearity (NIDL) of the oscilloscope [9].

Linear conductance quantization using the Landauer [14] approach is easy to justify [15] and calculations predicted conductance quantization [16]. However, a nonlinear theory for the conductance is not a settled issue. There have been predictions [17] of the development of a new step of half quantum (e^2/h) as the voltage is increased, and experimental work by Patel *et al.* [18] claims agreement with Glazman. However, there has also been criticism [19] based on numerical calculations for the conductance when eV $\gg E_f$. This is quite a complicated problem, and the solution depends on whether adiabatic transport takes place or not and how the behavior of the electron density in the high field region is created at the constriction. Possible scenarios are as follows: (i) Electrons accommodate in the constriction to the high fields, due to the applied bias voltage. In this case the relevant wavelength is that of the electrons at eV. (ii) The field produces band bending for a constriction narrower than λ_F and redefines the electron density at the constriction. (iii) The Fermi energy of Bi (rhombohedral structure with two atoms in the unit cell) depends on subtleties in the L point of the band structure in the bulk [7,8]. Perhaps when Bi is under stress and, defining a narrow wire, the Fermi energy is modified, a new gas density exists at the constriction with a redefinition of the effective mass [7,8]. Nevertheless, although there are stresses in the constriction, it should be mentioned that the section is of the order of 50 nm, much larger than that for metals [1–5]. (iv) The conduction is not totally ballistic and electrons travel ballistically from one bulk Bi reservoir to the constriction, accommodating in it, and then from the constriction gas into the other reservoir. This phenomena also produces CQ [20].

In conclusion, we have presented conductance experiments on Bi nanowires at 4 K. The conductance curves exhibit marked plateaus mostly at integer values of $2e^2/h$, as demonstrated by the histogram, and lasting about 50 nm electrode separation. The I-V characteristics present conductance breaks at half and/or integer quantum values.

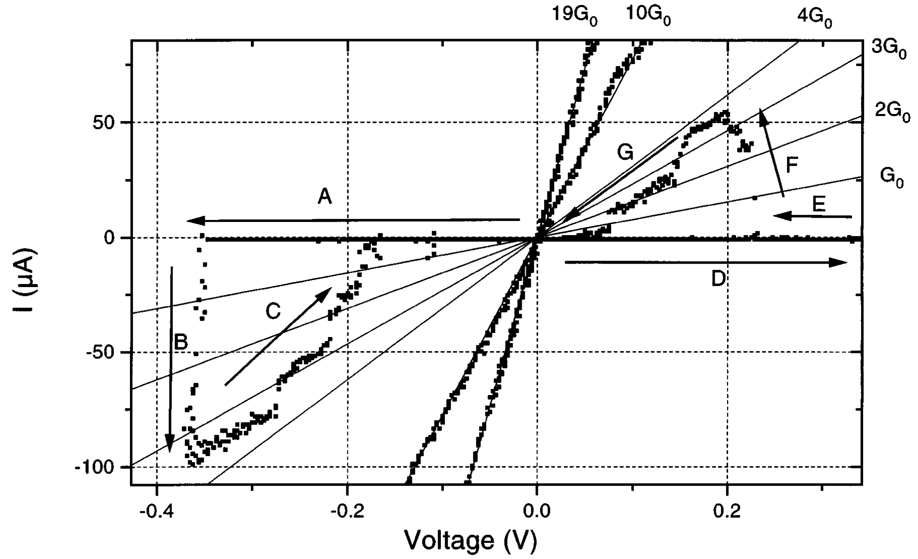

FIG. 4. *I-V* characteristic curves of Bi nanocontacts at 4 K. The tip is slowly retracted while sweeping the bias. Notice that for low conductance values there are marked conductance transitions. The applied bias evolution is indicated by the letters *A* to *G* in the low conductance *I-V* curve. Notice that initially the conductance is zero (*A*) but after a sharp increase in the conductance (*B*) the conductance decreases with marked transitions (*C*) back to zero. This behavior is observed again in the positive branch of this *I-V* curve, *D-E-F-G*.

This kind of behavior has not been observed in similar experiments with Au electrodes [5]. The data seem to indicate that the addition or removal of electronic states to the constriction can occur both when the size of the nanowire changes at constant bias or when the bias changes at constant size; i.e., the applied bias might play the role of a gate voltage.

The authors wish to thank Professor F. Besenbacher and co-workers for information about the nonideal differential linearity histogram correction. This work was supported by European Union (BRITE and ESPRIT), Spanish (DGCIT and CICyT), and Swedish (NFR and TFR) agencies.

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