Nanocontacts: Probing Electronic Structure under Extreme Uniaxial Strains

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Nanometer-sized metallic necks have the unique ability to sustain extreme uniaxial loads (about 20 times greater than the bulk material). We present an experimental and theoretical study of the electronic transport properties under such extreme conditions. Conductance measurements on gold and aluminum necks show a strikingly different behavior: While gold shows the expected conductance decrease with increasing elastic elongation of the neck, aluminum necks behave in the *opposite* way. We have performed first-principles electronic-structure calculations which reproduce this behavior, showing that it is an intrinsic property of the bulk band structure under high uniaxial strain. [S0031-9007(97)04623-1]

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The properties of solids under extreme strains are of great importance in fundamental and applied physics [1,2]. Large strains are present close to point and line defects, in semiconductor multilayers and thin films, and in mesoscopic devices like quantum wires and dots. The physics of liquids and solids under high *hydrostatic* pressures has long been a topic of study. In contrast, the study of *uniaxial* deformations is much more difficult because the attainable strains are severely limited by the appearance of plastic flow through the propagation of dislocations. Recently, it has been realized that nanometer-sized necks are much stronger than macroscopic samples, being able to sustain much higher strains [3–5]. This is because their small size keeps them essentially free of dislocations, and plastic deformation must take place via atomic rearrangements and slip of atomic planes [3,6]. Another essential difference between macroscopic and nanometer-sized systems is related to the nature of electronic transport. For all normal metals under pressure, the conductivity is determined by the pressure dependence of the electronic mean free path ℓ [1]. But, as the size of the structure becomes smaller than ℓ, transport becomes ballistic and the conductance is expected to be dominated by the electronic band structure itself.

It this report, we study the dependence of ballistic electronic transport with uniaxial elastic deformation. We present measurements of the conductance of nanometer-sized aluminum and gold necks, as well as first-principles electronic-structure calculations. In the case of Au the conductance decreases as the neck is elongated, which could be explained in terms of the lateral contraction of the neck with elongation. However, Al follows a most unexpected behavior: The neck conductance *increases* as it is elongated. This counterintuitive behavior is traced to the particular shape of the Fermi surface (FS) and its change with strain.

Nanometer-sized metallic necks can be fabricated using a scanning tunneling microscope (STM) [7,8] or the mechanically controllable break junction technique [9]. Our experimental procedure consists in forming a metallic contact between the STM tip and sample, both of the same metal. When the tip is retracted, a neck of controllable dimensions forms by plastic deformation. The experiments were done in a low-temperature STM. The measurement of the conductance shows clear steps, which can be quite repetitive for large contacts, as the neck is cyclically deformed [8]. In Fig. 1, we present typical experimental conductances for Al and Au nanometer-sized contacts as a function of the elongation. The conductance curves present no significant differences between low (4 K) and room temperature. The experiments show a striking and systematic difference between Au and Al: The slope of the plateaus differs in sign. This inverted slope has already been reported for Al contacts with a conductance G of the order of a few times the quantum of conductance $(2e^2/h)$ [10]. Since this implies necks of only a few atoms, it has lead some authors to suggest that the anomalous behavior might be related to chemical bonding [10] or scattering effects [11] at the atomic scale. However, this could not explain our results which are for values of G ranging from a few quanta to

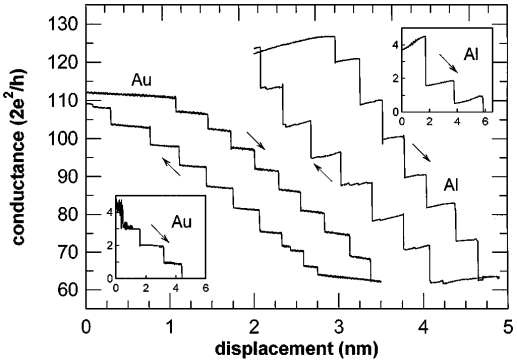

FIG. 1. Conductance vs tip-sample relative displacement for Au and Al, for contacts of about 100 atoms in cross section. The abrupt jumps are associated to mechanical relaxations (atom rearrangements), while deformation between two such relaxations is elastic. The insets show the behavior for very small contacts.

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several hundred (i.e., cross sections up to several hundreds of atoms).

The abrupt steps in the conductance have been shown to be correlated to abrupt force relaxations, by measuring simultaneously the conductance and forces in gold contacts [4]. The estimated critical pressure to produce an abrupt plastic yield was approximately constant and of the order of 4 GPa (i.e., a factor 20 times larger than in bulk materials [5]) as predicted by molecular dynamics simulations [3]. Between two successive relaxations, the deformation is elastic (reversible). For gold contacts the slope of these elastic stages is consistent with what would be expected from the elastic lateral contraction with elongation (i.e., the Poisson ratio) [12]. For Al, however, the observed variation has the opposite sign (even for the largest cross sections studied) and cannot be explained by that argument. The fact that this effect can be observed for rather large cross sections (hundreds of atoms) suggests that the origin of this behavior could be related to the properties of the *bulk* electronic structure.

We have performed first-principles electronic-structure calculations for both Au and Al under the extreme uniaxial strains of the experimental conditions. The cubic cells were elongated and compressed by different magnitudes in three crystalline directions: (100), (110), and (111). The deformation in the perpendicular direction (Poisson ratio) was included by calculating the deformation tensors [13] from the macroscopic elastic constants [14]. For each deformed cell we performed a standard density functional calculation [15], in the local density approximation for exchange and correlation [16]. We used a plane wave basis [17] and norm-conserving pseudopotentials [18] in its fully nonlocal formulation [19].

The shape of the constriction can be estimated from the evolution of the conductance as the constriction is deformed plastically [8]. For cross sections of the order of a hundred atoms, it is almost cylindrical with a smooth connection to the electrodes. The distribution of strain is approximately uniform within the length of the nearly cylindrical region of the contact (for Al contacts with $G \approx 100$ a length of ≈ 5 nm is estimated [8]). We then assume that the neck ballistic conductances can be calculated from the electron wave functions of the bulk deformed metal. To do this, consider two samples joined by a ballistic constriction of minimum cross section A. We approximate the current flowing from the right (I^R) and from the left (I^L) as

$$I^{R,L} = \frac{eA}{4\pi^3} \sum_i \int_{\mathrm{BZ}} d\mathbf{k}\, \frac{|\hat{\mathbf{n}} \cdot \mathbf{v}_i(\mathbf{k})|}{2} \quad f(\epsilon_i(\mathbf{k}) - \epsilon_F^{R,L}), \tag{1}$$

where e is the electron charge, $\hat{\mathbf{n}}$ is a unit vector normal to the cross section, $\epsilon_i(\mathbf{k})$ and $v_i(\mathbf{k})$ are the band energies and group velocities, $\epsilon_F^{R,L}$ is the Fermi energy at each side of the constriction, and $f(\epsilon)$ is the Fermi-Dirac distribution [20]. The integral is over the whole Brillouin zone (BZ), but the absolute value and the factor $1/2$ takes into account the electrons moving in one direction only. For a small applied voltage $V = |\epsilon_F^R - \epsilon_F^L|/e$, the conductance $G = |I^R - I^L|/V$ is given by $G = \sigma(\hat{\mathbf{n}})A$, where

$$\sigma(\hat{\mathbf{n}}) = \frac{e^2}{4\pi^3} \sum_i \int_{\mathrm{BZ}} d\mathbf{k}\, \frac{|\hat{\mathbf{n}} \cdot \mathbf{v}_i(\mathbf{k})|}{2} \left(\frac{\partial f}{\partial \epsilon}\right)_{\epsilon=\epsilon_i(\mathbf{k})-\epsilon_F}. \tag{2}$$

The group velocities are calculated [21] from the electron wave functions of the self-consistent potential. The convergence of the integrals with respect to the number of plane waves and $\mathbf{k}$ points was carefully tested [22].

Figure 2(a) presents the calculated conductances versus the strain of the sample $\Delta L/L_0$, in different crystalline directions. The conductance has been normalized to its value G_0 in the undeformed cell [23],

$$\frac{G}{G_0} = \frac{\sigma(\hat{\mathbf{n}})}{\sigma_0(\hat{\mathbf{n}})} \frac{A}{A_0}, \tag{3}$$

where $A/A_0 = [1 - R(\hat{\mathbf{n}})\,\Delta L/L_0]^2$ and $R(\hat{\mathbf{n}})$ is Poisson's ratio. For Au, our results reflect the expected decrease in the conductance as a function of the elongation of the contact. For Al, the results critically depend on the orientation. While, along the (100) direction, they present a qualitative behavior similar to Au, both the (110) and

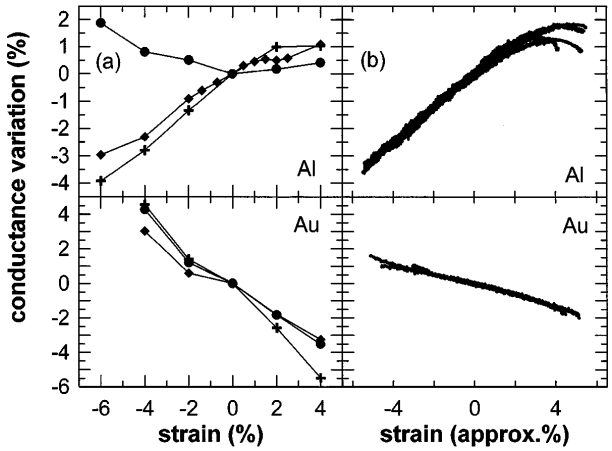

FIG. 2. (a) Theoretical variation of the ballistic conductance with strain. Positive and negative strains indicate elongation and contraction, respectively. Circles: (100); crosses: (111); diamonds: (110). The calculated values of $\Delta G/G_0$ are converged to better than 10%, with respect to the number of plane waves and $\mathbf{k}$ points. (b) Experimental variation of the conductance for elastic deformations. Many different experiments are plotted together. Notice that the vertical scale for the experimental curves is the same as for the theoretical curves, while the horizontal scale has been estimated from the maximum stress that the neck can sustain. In the case of Au, this has been measured experimentally and it is about 4 GPa. This implies (using Young's modulus E for Au) a relative deformation $\Delta L_{\max}/L_0 \sim P_{\max}/E \sim 5\%$ at the extremes of the curves. Preliminary measurements indicate similar values for Al.

(111) orientations show an anomalous increase of the conductance as a function of the elongation. Figure 2(b) shows the experimental variation of the conductance during elastic deformation. Although a direct quantitative comparison would require the knowledge of the relative elongation $\Delta L/L_0$ in the experiments, the calculated and experimental conductances are strikingly similar, providing confidence on the bulk origin of the conductance behavior. In the case of Al, the calculations suggest that the contacts are crystalline and oriented preferentially along the (110) or (111) directions.

The unexpected behavior of the Al conductance arises from a delicate interplay between the electron density of states and the group velocity at the FS. To get further insight into this interplay, we can take the zero-temperature limit of Eq. (2):

$$\sigma(\hat{\mathbf{n}}) = \left(\frac{2e^2}{h}\right)\frac{S(\hat{\mathbf{n}})}{4\pi^2}, \tag{4}$$

where $S(\hat{\mathbf{n}})$ is the area of the FS, projected on the plane normal to $\hat{\mathbf{n}}$ [in a free-electron picture $S(\hat{\mathbf{n}}) = (4\pi^3/\lambda_F^2)$, where λ_F is the Fermi wavelength, and we recover the classical Sharvin formula [24] $G = (2e^2/h)(\pi A/\lambda_F^2)$]. Since the d bands of Au are well below the Fermi level, its FS is entirely determined by its s band, and it is quite spherical and fully contained in the first BZ. Its total (unprojected) area S_T is only 0.5% smaller than that of the free-electron gas, with one electron per atom. It also behaves similarly with deformation, depending essentially of the resulting electron density. The case of Al is quite different: With three valence electrons, its FS extends into the third BZ. This implies a larger distortion from the free-electron FS, as it crosses the BZ boundaries many times. S_T turns out to be 21% smaller than the value predicted by the free-electron model. When Al is deformed, the shape of the Fermi surface changes while the total area S_T remains almost constant in contrast to the free-electron model. The anomalous behavior of the conductance under uniaxial strain in certain crystal directions is then due to changes of the *shape* of the Fermi surface.

Of course, the discussion above cannot be applied directly to very small contacts, where scattering by the neck walls is determinant and the contribution to the electric transport comes from a few discrete conductance channels. It is worth noticing, however, that the same experimental behavior is observed continuously from high to low conductance values (See Fig. 1). This suggests that the underlying mechanism of the conductance behavior in atomic-scale contacts may also be related to the effect of the uniaxial strain on the electronic properties of the contact (in this case, on the transmission probabilities through different channels). We expect that our work will stimulate further experiments and calculations in this direction.

In conclusion, we have presented conductance measurements on Au and Al necks. In the case of Al the experiments show an increase of the conductance as the contact is elongated elastically. This behavior is observed continuously for conductance values ranging from a few quanta to several hundred. Our first-principles electronic calculations show that, for large contacts, this behavior is an intrinsic property of the bulk band structure under high uniaxial strain. These results suggest that the conductance behavior in atomic-scale contacts may be also determined by the effects of the extreme uniaxial strains. Apart from its possible relevance on the development of nanoscaled electronic devices, our results show that the detailed electronic structure of a metal is essential to understand the ballistic transport through a metallic constriction, and that the free-electron model is generally not sufficient. Together, our experiments and calculations demonstrate that nanometer-sized metallic necks provide a new tool to study the effects of high uniaxial strains on the electronic structure and transport properties of solids.

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