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Electron scattering effects at physisorbed hydrogen molecules on break-junction electrodes and nanowires formation in hydrogen environment

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Physisorption of hydrogen molecules on the surface of gold and other coinage metals has been studied using distance tunneling spectroscopy. We have observed that the distance dependence of the tunnel current (resistance) displays a strong N-shaped deviation from exponential behavior. Such deviations are difficult to explain within the Tersoff–Hamann approximation. We suggest the scattering of tunneling electrons by H_2 molecules as an origin for the observed effect. We have found that this phenomenon is also common for strongly adsorbed organic molecules with a single anchoring group. Pulling Au, Cu and Pt nanowires at 22 K in hydrogen environment shows that the break-junction electrodes are still connected through hydrogen–metal monoatomic chains down to very low conductance values of 10^{-4}–10^{-6} G_0. © *2012 American Institute of Physics.*
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1. Introduction

The idea to build electronic devices based on single molecules dates back to 1974 (Ref. 1) when the concept of a molecular rectifier was put forward. However, realistic experiments on conductance through a single molecule placed between metallic electrodes started 25 years later, when the modern techniques were able to produce stable atomic-sized contacts. These techniques include the Mechanically Controllable Break-Junction (MCBJ) method, which is widely used in studies of the molecular junction conductance (see reviews Refs. 2–4 and references therein).

It is not surprising that the behavior of a hydrogen molecule between the electrodes of MCBJ was studied very extensively due to the simplicity of the object. Most of the experiments were performed using transition metals. On many occasions the interaction of hydrogen with the surface of those metals is accompanied by molecular dissociation, even at low temperatures, and is highly material specific. Conductance of approximately one quantum unit $G_0 = 2e^2/h$ ($1/G_0 \approx 12.9$ kΩ) through the hydrogen bridge between Pt electrodes were reported in Ref. 5. In the case of Pt (and, most probably, of ferromagnetic metals too[6]) the hydrogen atoms can only be found on the surface and the hydrogen bridge retains some of the properties of the H_2 molecule.[5,7,8] For Pd,[9] however, the underlayer of hydrogen distinctly changes the conductance through the hydrogen bridge. For W, Mo and Ta the dissociation of H_2 molecules is quickly followed by dissolving of the hydrogen atoms (protons) into the electrodes via quantum diffusion. This effect drastically changes the conductance properties of the electrodes and eventually makes measurements of the contact conductance practically impossible.[10,11]

For gold the strong interaction between the adsorbed molecules of hydrogen results in perceptible changes in the individual conductance traces measured at disconnection of the electrodes and therefore in conductance histograms. This includes the appearance of the additional "fractional" peaks when measured in hydrogen environment[12] and incorporation of the hydrogen molecules ("hydrogen clamp") in the monoatomic chains. The latter effect results in reduction of the chain conductivity and emerging of a periodic structure in the conductance curves.[13]

The reason for the observed effect is the strong reactivity of the gold nanowires predicted in Refs. 14 and 15. The strong interaction between gold nanoclusters and hydrogen was reported in Ref. 16 and the potential applications of gold nanostructures as catalysts, biochemical sensors etc. are widely discussed in Ref. 17.

In this article we report measurements of the conductance effects of a physically adsorbed hydrogen molecule in a MCBJ. This effect can be detected with the distance tunneling spectroscopy (DTS) method by measuring the contact conductance as a function of the gap z between the electrodes.[18] The first experiments related to DTS were done on physically adsorbed He (Ref. 19) and the deviation of the tunneling conductance $G(z)$ from exponential behavior was attributed to the strong reduction of the electron density of states close to the Fermi level by adsorbed atoms of helium predicted by Lang.[20] The same argument is given for scanning tunneling hydrogen microscopy (STHM) contrast of a

gold dimer on a gold surface,[21] where on top of the dimer (smaller tunneling gap) the conductance is lower than on the edge. Weiss *et al.*, argue that this is caused by depletion of the local density of states due to the Pauli repulsion between electrons in the metal and the electrons of the deuterium molecule in the gap. On the other hand, the oscillating behavior of the tunnel current $\lg I(z)$ ($\lg I(z) \equiv \log_{10} I(z)$) observed upon moving the STM tip in the direction perpendicular to the adsorbed layers of H_2O was explained by the variation of the tunnel barrier height φ in a rather wide range between 0.8 and 2.4 eV.[22] Both explanations were consistent with the Tersoff–Hamann (TH) approximation.[23] Some situations, however, e.g., heterogeneous sub-nanoscale environment could need approaches beyond the scope of the TH approach.

The data we are presenting here seem unlikely to be explained by a straightforward TH approach, as this would mean an increase of the barrier height to roughly 10 eV, or a depletion of the density of states by about two orders of magnitude. We propose a simple model based on the electron scattering by physically adsorbed H_2 molecules that might explain the observed effects.

Additionally we have found that the similar dependences of the tunnel conductance $G(z)$ are characteristic for organic molecules with a single anchoring group. In the direct contact regime, the pulling characteristics for Au, Cu and Pt are strikingly different from those observed for Au in Ref. 13.

2. Experiment

In our experiments we have used a standard MCBJ technique described elsewhere.[24] All measurements have been done either in a cryogenic ultra-high vacuum or in the atmosphere of ultra-pure (99.9999%) hydrogen. The vacuum pot with the sample has been cooled by pumping of He vapor through a special transfer tube with a regulated input, in the way similar to that used in flow cryostats. In spite of the relatively low absolute accuracy of the Allen-Bradley carbon resistor thermometer we used for temperature readings (the error of the calibration curve at the temperatures of about 20 K can be as large as ± 0.2 K), we were able to maintain the temperature of the sample within ± 0.01 K for sufficiently long time (up to 3–4 h). Normally, the vacuum pot was initially overcooled by ≈ 1–2 K and the desirable temperature was maintained with a heater, monitored by a Lake Shore 340 temperature controller. The thermal drift of the electrodes in the tunneling regime usually was less than 2–3 pm per minute.

All measurements presented below were done at 22 K (above the boiling point of hydrogen 20.268 K). We found that the effects reported below are rather insensitive to the amount of hydrogen admitted into the vacuum pot and can be observed at hydrogen pressures (measured at the top of cryostat) ranging from 10^{-3} to 100 Torr.

3. Results and discussion

3.1. Scattering of electrons by the hydrogen molecule

The most spectacular curves of the contact conductance versus interelectrode separation z measured in the quantum conductance units $G_0 = 2e^2/h$ for Au MCBJ are presented in Fig. 1.
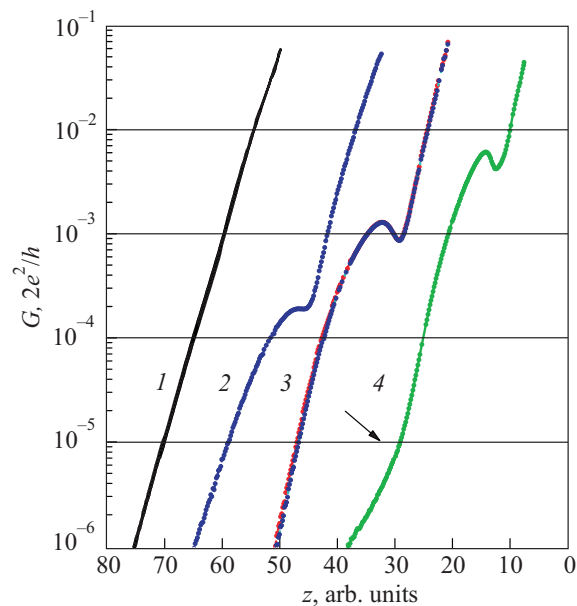

FIG. 1. Typical dependences of the contact conductance G versus electrode separation z for a Au MCBJ in vacuum (curve *1*), and in case of physically adsorbed H_2 (curves *2–4*). The last dependence shows the possible presence of a second layer of adsorbed hydrogen molecules (or the presence of a molecule adsorbed on the "sharp" electrode) at G dependence around $10^{-5}G_0$ (indicated by the black arrow).

Under cryogenic UHV condition this dependence demonstrates a perfect exponential behavior in the entire range of conductances (curve *1*). Admitting even a small ($\sim 0.5 \mu$M) amount of hydrogen results in a strong deviation of $G(z)$ from the exponential behavior. All curves presented in Fig. 1 were measured in the process of approaching the electrodes to each other up to a conductance less than 0.1 G_0 (thereby avoiding a jump to the direct contact due to metallic adhesion) and some of them also in the reverse process of subsequent withdrawal of the electrodes (curves *1, 3*). In the most cases the resulting dependences are practically identical. Compared to our measurements on physisorbed He,[19] the effect of adsorbed hydrogen molecules on the tunnel conductance is much stronger. The tunnel current reaches the maximum and then decreases as the distance between the electrodes continue to decrease (curves *2–4*). This singularity usually occurs in the range between 10^{-2} and 10^{-4} G_0. The spread in the data is probably related to the variation in the position of the adsorption potential minimum for H_2 at specific adsorption sites on the rough surface of the electrodes (in some respects similar to the top, hollow or bridge adsorption sites on a metallic surface). We assume that these N-shape signatures in the curves presented in Fig. 1 correspond to the situation when a hydrogen molecule adsorbed on the "blunt" electrode is located directly opposite (or slightly shifted) to the foremost atom of the "sharp" electrode. In other cases the distortion of the $\lg G(z)$ curves is less pronounced and reduced to a "plateau". Fig. 2 shows the transformation of those dependences due to the thermal drift of the electrodes (with a switched off feedback circuit of the temperature controller) in z and lateral directions. The estimated drift in z and/or lateral direction does not exceed 1–2 Å.

The bias dependence of the $\lg G(z)$ curves was observed before in the case of the physically adsorbed helium.[19] In a
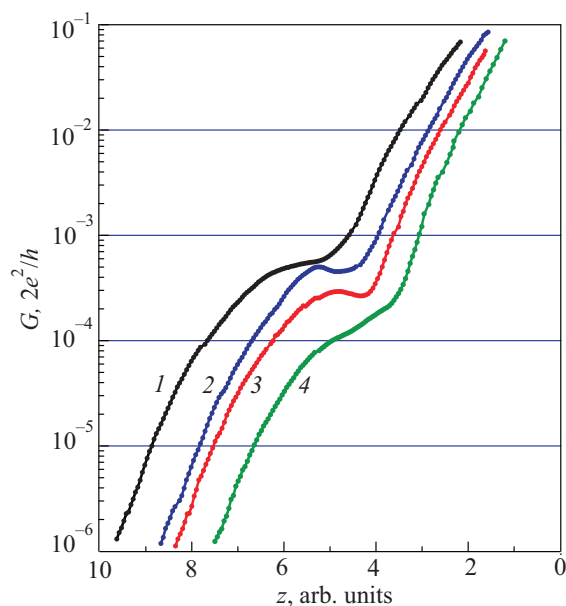
FIG. 2. Evolution (from left to right) of $G(z)$ dependences in the course of the thermal drift of the electrodes as the temperature drops from 22 to 21.7 K with feedback switched off.

rather narrow range of V_b (1–20 mV) the deviation from exponential behavior increased with the decrease of bias voltage. This effect could not be properly explained at that time. For adsorbed hydrogen molecules the influence of V_b on the shape of $\lg G(z)$ curves can be observed in a higher bias range up to 100 mV (Fig. 3). At even higher bias voltages the contact conductance becomes unstable and shows a sudden jump (see inset in Fig. 3). At $V_b > 500$ mV any recording of $\lg G(z)$ is already practically impossible. Due to a relatively high polarizability of the hydrogen molecule, the instability starts at estimated field strength of 0.02–0.05 V/Å, whereas in the case of adsorbed He, the measurements at the field strength as high as 0.5 V/Å were still possible.
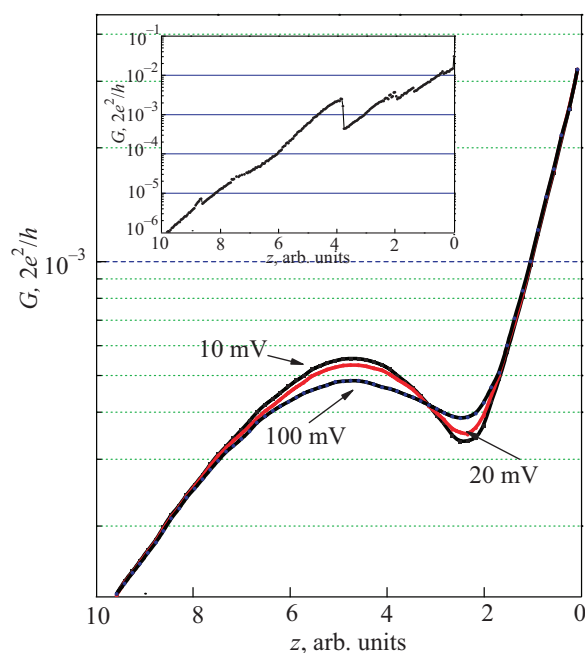

FIG. 3. Part of the $\lg G(z)$ dependence for the same junction at different bias voltages. Inset: unstable $G(z)$ curve measured at $V_b = 400$ mV.

The measurements on Ag, Cu and Pt show clear deviation of $G(z)$ dependences from exponential behavior. However, this effect is less pronounced than in the case of Au. It should be remarked that the conductance value corresponding to the singularity in $\lg G(z)$ curves cannot be viewed as a "conductance" through a hydrogen molecule, as in this case it does not form chemical bonds with the electrodes.

As stated above the N-shaped $\lg G(z)$ curves are not easily explained using the TH model. Otherwise one must accept either a reduction of electron DOS by 1–2 orders of magnitude or a sudden few fold increase of the tunnel barrier height φ. The above results suggest that the most plausible explanation for the effect observed might be scattering of the tunneling electrons by a hydrogen molecule. At relatively large separations between the electrodes (5 to 7 Å) the scattering is relatively small. As the distance between the electrodes decreases, the percentage of tunneling electrons scattered by the impenetrable hydrogen molecule rapidly increases. At a certain moment this results in the reduction of the tunnel current until the moment the repulsive Pauli potential starts to expel the H_2 molecule from the tunnel gap. In Sec. 3.2 we use a simple model to reproduce in a simulation the observed N-shape deviation described above.

3.2. Simple simulations

The exact description of the observed effects requires a quantum mechanical approach and rather complicated calculations. However, the main features of the $G(z)$ dependences can be described qualitatively using a very simple classical model presented in Fig. 4. This involves only geometrical considerations. In this model we assume that one of the electrodes is atomically flat on the scale of a few interatomic distances while the second one is atomically sharp. The hydrogen molecule is represented by an impenetrable for electrons sphere of diameter d at the distance $P \sim 2.5$ Å from the flat electrode (for the majority of metals the distance between the surface and the physisorbed molecule is 2.3–2.7 Å (Ref. 25)). The parameter Z_{push} represents the distance at which the expelling of the molecule starts, as the separation between the electrodes decreases, and is held at 4.5–5 Å. The distance Z_{push} of electrode 2 at which expelling of the hydrogen molecule from the interelectrode space begins is at the deepest point of the potential well in the adsorption potential curve. For Au, Ag and Cu, the well is approximately 30 meV deep.[26] The expelling of the H_2 molecule is done in a linear way, for every step electrode 1 takes towards electrode 2 the molecule is expelled a step along the plane of electrode 2 (i.e., perpendicular to the z-axis). We
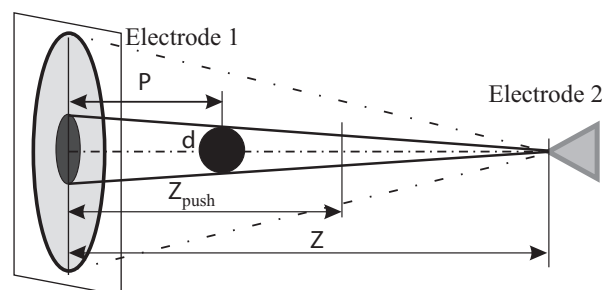

FIG. 4. Simple model for electron scattering on a H_2 molecule. The shadowed area on electrode 2 represents the amount of backscattered electrons.

also suggest that only electrons in the cone with solid angle of 30° are contributing to the conductance. As the distance between the two electrodes is decreased, the amount of back-scattering by the hydrogen molecule increases. This is modeled by an increase in the "shadow" of the molecule on electrode 2. Under the above parameters, a satisfactory agreement with the experiment can be found assuming that the effective scattering radius is 0.5–0.6 Å. For the diameter d it gives 1.0–1.2 Å for d and correlates with the small dimension of a hydrogen molecule (the distance between protons is 0.74 Å).

3D plots of the $G(z)$ dependences are presented in Fig. 5 as a function of the pushing distance Z_{push} assuming the scattering radius R_{scatt} to be equal to 0.55 Å (Fig. 5(a)) and as a function of scattering radius at $Z_{push} = 4.8$ Å (Fig. 5(b)). The simulated characteristics clearly reproduce the effect of conductance reduction observable in a relatively narrow range of Z_{push} and R_{scatt}, respectively.

In the case when the hydrogen molecule is shifted away from the contact axis, the effect of conductance reduction disappears rather fast (curves *1* and *2* in Fig. 6). This correlates with the fact that the experimental observation of this effect occurs only for 5%–10% of all curves measured. The simple model of scattering shows qualitatively the same
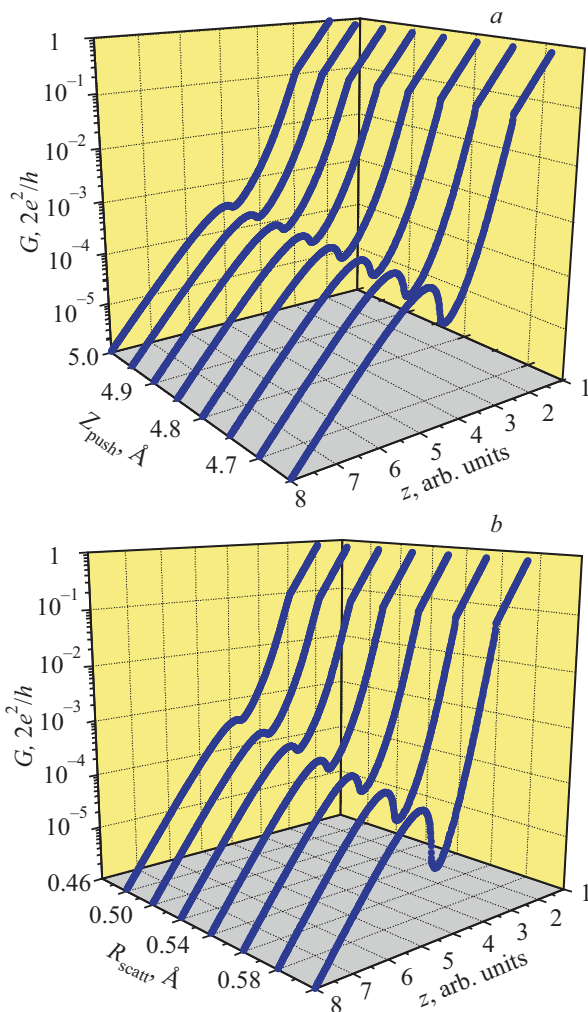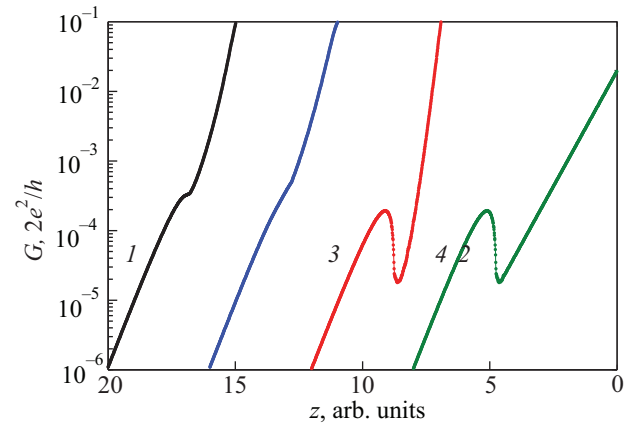

FIG. 6. Conductance curves *1* and *2* are simulated for the hydrogen molecule shifted from the contact axis by 0.1 and 0.2 Å. Curves *3* and *4* correspond to increase and reduction of the metal work function after expelling the hydrogen molecule from the interelectrode space.

trend as observed in the data, however, is unable to explain the apparent increase of the tunneling gap (Fig. 1). This effect can be understood only if we suggest that some of the tunneling parameters in TH approximations are not constant and changing with z. It is a well-known fact that the adsorption of hydrogen on the surface may reduce or increase the work function of the metal. This effect is included in curve *3* (increase) and *4* (reduction of the work function) in Fig. 6 after the molecule is pushed out. The effect of electron scattering is not limited only to physically adsorbed hydrogen but bears a universal character and can be observed on other sufficiently strongly adsorbed molecules. To prove it we studied the conductance traces of 1-pentanethiol and thiophenol chemisorbed on the electrodes of gold MCBJ. These measurements were done at room temperature in 1,2,4-trichlorbenzene. (For experimental details of such measurements see Ref. 27.)

We were able to detect the presence of 1-pentanethiol and thiophenol at concentration as low as 10 nM. Typical individual conductance curves show N-shaped behavior and contribute to a distinct peak in the conductance histogram presented in the lower panel of Fig. 7. However, the position of the anomaly on individual conductance curves, and therefore position of the maximum in the conductance histogram, may change within 1 to 2 orders of magnitude. Therefore, it is impossible to identify the molecules by a single conductance value. However, the measurement is sufficiently sensitive for the detection of molecules on the surface, by identification of an N-shape in the conductance curves.

3.3. Pulling the nanowires in molecular hydrogen environment

All the measurements for hydrogen molecules presented above have been done in the tunneling regime without bringing the electrodes into direct mechanical and electrical contact. In this section we present the conductance traces measured in the course of pulling electrodes, starting from direct contact with the conductances of 10–20 G_0. It was shown in Ref. 13 that a hydrogen molecule can be included in a single-atom nanowire clamping to neighboring gold atoms. At temperatures starting from 4.2 K and below 10–15 K our results for pulling gold nanowires coincide nicely with these

FIG. 5. 3D plots for the families of $G(z)$ dependences as functions of the pushing distance Z_{push} assuming the scattering radius R_{scatt} equal to 0.55 Å (a) and as functions of the scattering radius at $Z_{push} = 4.8$ Å (b).
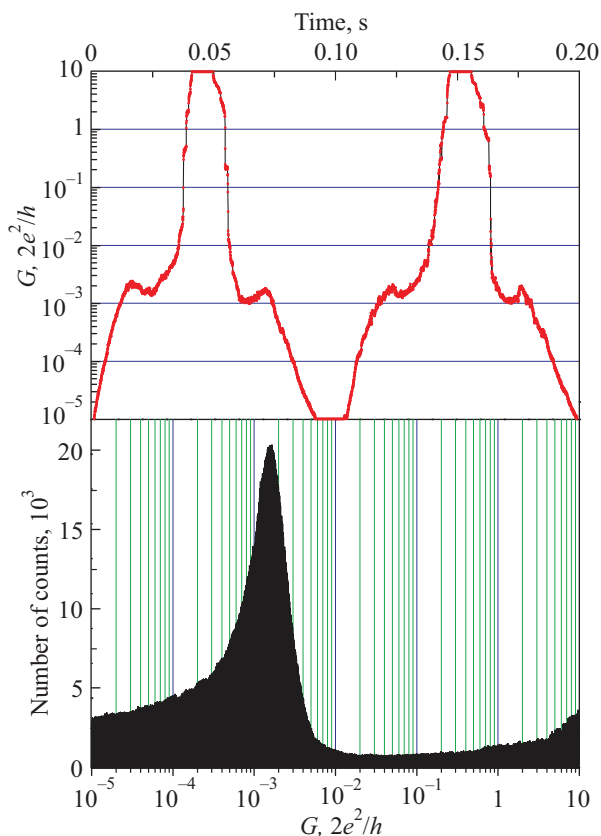
FIG. 7. Conductance traces for adsorbed thiophenol molecules, measured with a 10 Hz triangle ramp piezovoltage (a). Conductance histogram constructed from 2000 individual traces (b).
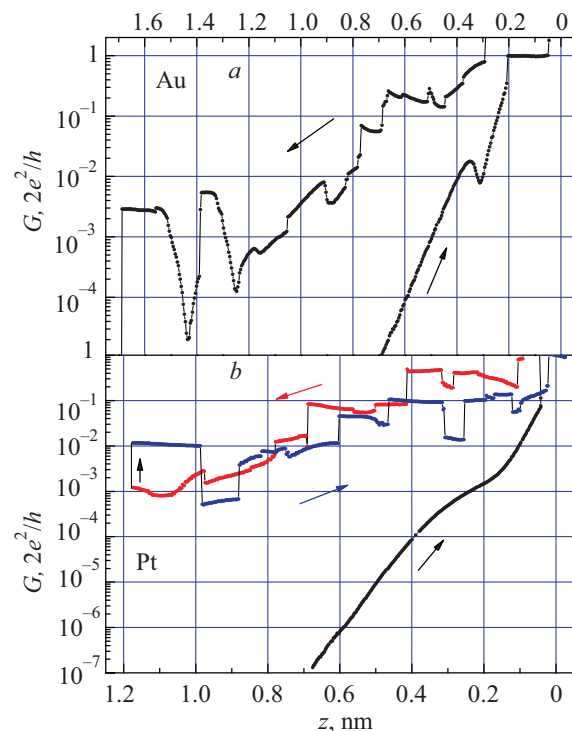

FIG. 8. Typical conductance curve for a gold MCBJ, on approach to the direct contact and, subsequent pulling of the nanowire (a). Pulling curves for Pt (b).

data. The distance between the electrodes was calibrated using either $G(z)$ dependences measured in UHV or the linear part of $G(z)$ curves measured in a hydrogen environment. Assuming that the work function values for Cu, Au and Pt are between 4.5 and 5.5 eV we can safely use a coefficient as (1 ± 0.1) Å per decade of conductance decay for calibration.

However, at higher temperatures (and an enhanced amount of hydrogen) the behavior of the conductance curves changes dramatically. Moreover, hydrogen-metal conducting chains can be pulled from Cu which does not form monatomic chains under UHV conditions. Like in the measurements presented above, the temperature was 22 K and the pressure of hydrogen 50 Torr. It should be noted also that the pulling speed in most of the experiments was usually less than 1 nm/min. A typical pulling curve for gold is presented in Fig. 8(a) and shows that the electrodes stay connected at distances as large as ~1.5 nm or approximately 5 interatomic distances. The conductance of the atomic chain drops as low as 10^{-5} G_0, or more than 3 order of magnitude below the conductances reported in Ref. 13. Like in Ref. 13 the conductance decreases in a non-monotonic way, with sudden drops and subsequent recovery sometimes even to higher values of G. This effect was explained in Ref. 13 on the assumption that the conductance through the hydrogen molecules stretched parallel to the contact axis is higher than for molecules oriented perpendicular to it. This assumption is based on simulations[15] where the conductance through a gold dimer welded by a hydrogen molecule was calculated. The rich structure of $G(z)$ curves in our experiments and the low conductance of the atomic chain indicate that more than

one H_2 molecule are incorporated into the nanowire in different configurations including probably "hydrogen wire" configurations with conductances as low as $0.01G_0$. Possibly, this is mainly due to the elevated temperature of the experiment and high hydrogen pressure that ensures high mobility and immediate availability of H_2 molecules along the atomic chain. It is likely that the low pulling speed also contributes to the observed effects. On rare occasions the conductance curves demonstrated quasiperiodic structure although a lack of reliable statistics prevents us from drawing parallels with the observation reported in Ref. 13.

We found that the "hydrogen clamp" also works for some other materials. Not surprisingly, it occurs for silver which is known for the possibility to pull short chains at cryogenic UHV condition and long chains in the presence of oxygen.[28] The conductance curves of silver are similar to those of gold. Platinum also forms monoatomic chains under UHV conditions.[29] Evidence that hydrogen molecules can be incorporated in the monoatomic chains of Pt atoms was presented in Ref. 30. Like in Ref. 13, these measurements were done at 4.2 K and in the limited range of conductances below G_0. In our case the $G(z)$ pulling curves for Pt look somewhat different (Fig. 8(b)). They consist mainly of flat or slightly tilted plateaus interchanged with the abrupt jumps in conductance (up and down) of approximately one order of magnitude. This difference in conductance behavior can be explained by the fact that at 22 K the dissociation of hydrogen molecules is quite probable and a hydrogen atom (proton) can be incorporated into the monoatomic chain. For gold such a situation results in a so-called "Hydrogen Switch" reducing the wire conductance to zero.[15] For Pt the conductance through a single hydrogen atom is still possible and most probably has little or no dependence on stretching

(in contrast to the hydrogen molecule). That explains the flatness of the plateaus in the conductance curves (Fig. 8(b)). The transition from pulling the Pt wire to its compression is usually accompanied by an immediate jump in conductance at the return point. As we continue to compress the nanowire, the character of $G(z)$ dependence remains generally the same until the final transition to direct metallic contact. Note that the "pulling distance" and the "return distance" are practically the same and therefore the process is completely reversible.

For copper (in contrast to gold, silver, platinum or iridium) the monoatomic chains have never been observed under UHV conditions, although according to Ref. 28 such an effect is possible under an oxygen atmosphere at elevated temperatures. Fractional conductance of gold and copper has been observed for nanocontacts in solution under electrochemical potential control in the range of hydrogen evolution.[31] Theoretical analysis performed in Ref. 32 demonstrated that a Cu nanowire can be rather reactive to hydrogen. In our experiments we observed two distinct types of copper nanowire behavior.

Some of the contacts demonstrated the pulling curves that were also characteristic both for Au and Ag with an unavoidable break at conductances of 10^{-3}–10^{-4} G_0 (see Fig. 9(a)). For other curves the final break to zero conductance did not occur until $G \sim 10^{-6}$ G_0 (Fig. 9(b)) and, for a larger part, the contact conductance decreases in a gradual way. The difference between these two types of dependences might very well be related to the crystallographic orientations of the electrodes. It is also possible that hydrogen molecules can be incorporated into the other parts of the electrode surface besides the monoatomic chain. In conclusion, we found that the deviations of $\lg G(z)$ curves from exponential behavior in the presence of hydrogen physisorbed on the surface of MCBJ electrodes cannot be easily explained within the framework of Tersoff-Hamann approximation by varia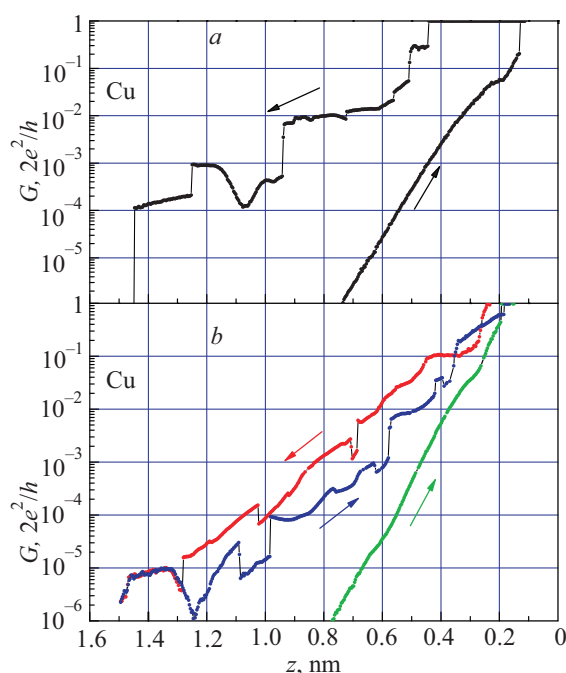tion of the electron DOS in the electrodes or the tunnel barrier height φ. We propose that a plausible model for the observed effects is the backscattering of tunneling electrons by the hydrogen molecule.

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FIG. 9. Two types of conductance curves for copper MCBJ on approach to direct contact and subsequent pulling of the nanowire.

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