

Conductance of Pd-H Nanojunctions

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Results of an experimental study of palladium nanojunctions in a hydrogen environment are presented. Two new hydrogen-related atomic configurations are found, which have conductances of ~ 0.5 and ~ 1 quantum unit ($2e^2/h$). Phonon spectrum measurements demonstrate that these configurations are situated between electrodes containing dissolved hydrogen. The crucial differences compared to the previously studied Pt-H₂ junctions and the possible microscopic realizations of the new configurations in palladium-hydrogen atomic-sized contacts are discussed.

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In recent years, great progress has been achieved in understanding the conduction properties of matter at the atomic scale. A large variety of experiments performed by scanning tunneling microscopes and the mechanically controllable break junction (MCBJ) technique have provided a comprehensive picture about the nature of conductance in monoatomic metallic junctions [1]. Even more recently, it was shown that these techniques can also be used to investigate the conductance through *molecules* between metallic electrodes [2,3]. Such measurements, however, are strongly influenced by the interaction between the molecule and the electrodes, and this interaction is poorly controlled in the experiment. Furthermore, it is difficult to make certain that a single molecule forms the junction.

Promising results have been achieved by studying junctions with the simplest molecule, H₂. It was shown by Smit *et al.* [4] that a single hydrogen molecule can form a stable bridge between platinum electrodes, which has a conductance of one quantum unit ($G_0 = 2e^2/h$), carried by a single channel. This configuration is naturally created during the rupture of a platinum nanojunction placed in the H₂ environment. The conductance of this molecular bridge is not an intrinsic property of H₂, but it results from the fine details of the connection to the electrodes. Therefore, both the atomic arrangement created by the hydrogen and its conductance are expected to be material dependent. For instance, in gold junctions a new atomic configuration with a conductance of $\sim 0.5G_0$ arises, which has been related to an atomic Au wire distorted due to the adsorption of hydrogen [5].

The interaction of hydrogen with the atomic-sized contact is an especially interesting problem for palladium junctions, as Pd is highly reactive with respect to H₂. Smit *et al.* [4] have noted in their study on the Pt-H₂ system that Pd behaves similarly in hydrogen surrounding as the isoelectronic platinum. Our present work, however, shows that the palladium-hydrogen system has a more complex

behavior, which is attributed to the dissolution of hydrogen in the electrodes.

We have performed measurements on high purity Pd samples. The contacts were created by the MCBJ technique in a cryogenic environment. The junctions were studied by conductance histograms [1], which are constructed from conductance vs electrode separation traces recorded during thousands of ruptures. The peaks in the histogram reflect the stable atomic configurations of the junction.

The conductance histogram of Pd measured in high vacuum is presented in Fig. 1(a). It shows a well-defined peak at $G \approx 1.8G_0$ corresponding to the conductance of a monoatomic Pd contact, which can have up to five partially open conductance channels [6]. The shape of the histogram is insensitive to the experimental parameters (bias voltage and temperature) in the range of the measurements ($V = 10\text{--}300$ mV, $T = 4.2\text{--}30$ K).

A remarkable change is observed in the histogram if a small amount of H₂ is admitted to the vacuum pot [7]. Because of the presence of hydrogen, the peak characteristic to a single-atom Pd contact disappears, and two new peaks appear in the histogram at $\sim 0.5G_0$ and at $\sim 1G_0$, respectively [Fig. 1(b)]. We note that the first peak has a rather indefinite position in the region $\sim 0.3\text{--}0.6G_0$. The second peak at $\sim 0.9\text{--}1G_0$ may disappear if the amount of hydrogen is increased, as shown in Fig. 1(c).

These histograms demonstrate that two new stable atomic configurations arise due to the adsorption of hydrogen on palladium contacts. The relation of these two configurations to each other can be studied by statistical analysis following the method introduced in our previous work [5]. We found that these two configurations are uncorrelated, which means that the appearances of the first or the second configuration during the same rupture are independent events. It shows that both configurations arise between the same electrodes, but the appearance of the configuration at $\sim 1G_0$ neither helps nor hampers the

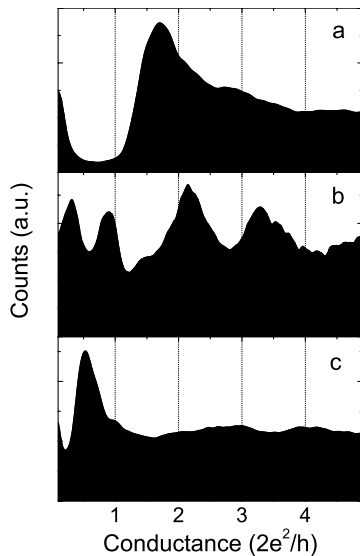


FIG. 1. Conductance histograms for clean Pd junction (a) and Pd in hydrogen atmosphere (b), (c) measured at $V = 150$ mV and $T = 5$ K.

appearance of the configuration at $\sim 0.5G_0$ during further retraction.

Additional information about the conductance channels of the configuration at $\sim 1G_0$ can be obtained by conductance fluctuation measurements. In Pt junctions, the suppression of quantum interference at $1G_0$ gave evidence that the hydrogen-related configuration has a single conductance channel [4]. As a sharp contrast, we have found that in Pd junctions the conductance fluctuations are not suppressed (see Fig. 2); thus, the configuration with $G = 1G_0$ has more than one open channel.

We have studied the structure of the electrodes around the new atomic-sized configurations as well. After pressing the electrodes together to a mesoscopic size ($\approx 100G_0$), the vibration modes of the junction were determined from the point contact (PC) spectrum [8],

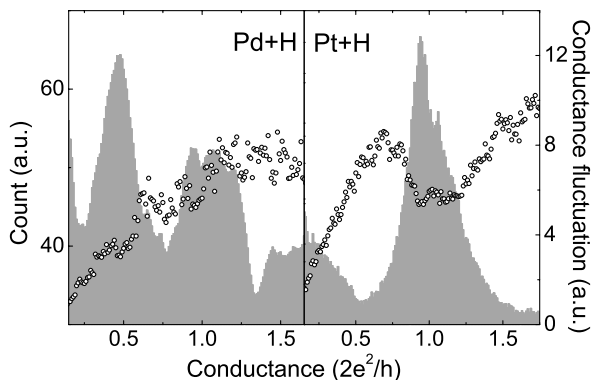


FIG. 2. The left panel shows the conductance fluctuation measurement on Pd-H junctions exhibiting both new configurations. As a reference, the conductance fluctuation in Pt-H contacts is shown in the right panel. In the background, the conductance histograms are presented for the same data sets.

i.e., the second derivative of the I - V curve recorded by the standard lock-in technique.

The PC spectrum for pure Pd [Fig. 3(b)] shows a single spectroscopic peak at $V \approx 15$ - 20 mV, which corresponds to the phonon modes of the Pd crystal in agreement with earlier results [9]. In contrast, in the presence of hydrogen [when the histograms of Figs. 1(b) and 1(c) are observed], the PC spectrum takes a significantly different form [Fig. 3(d)]. In this case, the spectrum is dominated by a wide peak at ~ 60 mV (arrow 1) along with a peak corresponding to the phonon modes of the pure Pd crystal (arrow 2). As a third feature, a zero bias anomaly is also observed (arrow 3).

These results can be compared with the observations on Pt contacts, where the vibrational spectrum of a H_2 molecular bridge (Fig. 2 in Ref. [4]) shows a closely similar structure to the PC spectrum in Fig. 3(d). To this end, we have performed measurements on mesoscopic-sized Pt junctions as well [see Fig. 3(f)], which were insensitive to hydrogen. These measurements show that in Pd contacts the presence of hydrogen is not only reflected by the new conductance values of atomic-sized junctions, but it is also markedly shown by the bulk properties of the electrodes. In contrast, in Pt contacts the hydrogen acts only on the surface.

Both Pd and Pt are well known for the chemical adsorption of hydrogen on the surface. In palladium

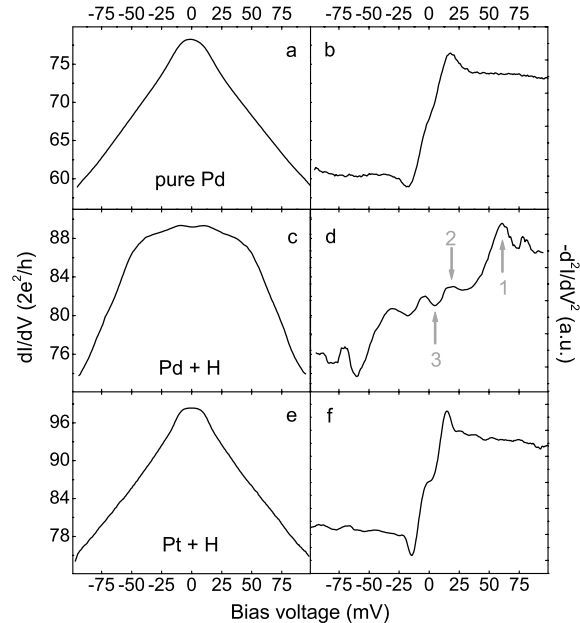


FIG. 3. The left/right panels show the first/second derivative of the $I(V)$ curves for mesoscopic junctions of pure Pd [(a) and (b)], Pd in hydrogen atmosphere [(c) and (d)], and Pt in hydrogen atmosphere [(e) and (f)]. In Pt the spectrum is unaffected by hydrogen; a similar curve is obtained for a pure Pt contact. The derivatives were measured simultaneously with a lock-in technique using a modulation of 2 mV at $T = 5$ K.

contacts, however, the hydrogen can also be dissolved in the bulk crystal due to the larger space at the octahedral interstitial sites in the fcc lattice. Indeed, the spectroscopic peak at ~ 60 mV in Pd junctions coincides with the vibrational modes of dissolved H atoms in the Pd host, in accordance with theoretical calculations [10], neutron scattering experiments [11], and PC spectroscopy measurements [12] on a palladium-hydride system (for an overview, see Ref. [13]). The zero bias anomaly in the PC spectrum could also be explained by the dissolved hydrogen [14].

Based on the above PC spectroscopy measurements, one can conclude that the new hydrogen-related configurations in Pd junctions are emerging between electrodes containing dissolved hydrogen. On the other hand, it should be emphasized that under our experimental conditions the dissolution of hydrogen is not expected, since the hydrogen is admitted to the contact *in situ* at low temperatures ($T < 20$ K), where its diffusion in Pd is completely frozen out [13]. For comparison, we have also performed measurements on samples that were cooled down after intentional dissolution of H at room temperature. These experiments provide the same PC spectrum as those where the hydrogen is added at cryogenic temperatures. We attribute the unexpected dissolution of H at low temperatures to the local overheating of the junction by the bias voltage. In the voltage range of the measurements (~ 150 mV), the contact is easily heated up to $T \sim 100$ K [15], where the hydrogen already has a reasonable diffusion rate (~ 1 nm/s) [13]. The repeated ruptures and compressions of the contact during the acquisition of the histogram may also assist the dissolution of hydrogen from the contact surface.

The amount of H dissolved in the contact is regulated by the balance of two parameters: the mobility of hydrogen in the Pd host and the partial pressure of H_2 gas near the junction. The mobility is controlled by the local overheating, whereas the H_2 pressure is determined by the amount of hydrogen in the sample space and the bath temperature. At $T = 4.2$ K the hydrogen is frozen; thus, its partial pressure is very small (10^{-6} mbar). The amount of hydrogen gas can be increased significantly by elevating the temperature to 20 K (the boiling point of hydrogen). If a high bias (> 200 mV) is combined with low bath temperature (4.2 K), then the cryogenic vacuum pumps out the mobile hydrogen from the junction. In this way, the situation with adsorbed hydrogen [histograms (b) and (c) in Fig. 1] can be turned into the case of pure palladium [histogram (a) in Fig. 1]. After this the electrodes can be “refilled” with hydrogen by increasing the temperature to 20 K. As the hydrogen is admitted to the junction, an intermediate state can also be observed for a few minutes. In this case, the presence of hydrogen at the contact is already reflected by the growth of a single peak in the histogram at $G = 1G_0$; however, the hydrogen is not yet dissolved in the electrodes, which is

clearly visible in the PC spectroscopy measurements on mesoscopic junctions.

Summarizing the experimental results, in palladium junctions two new stable atomic configurations arise due to the adsorption of hydrogen at $G \sim 0.5G_0$ and $G \sim 1G_0$. These two configurations can independently appear during the same rupture, between the same electrodes. According to the phonon spectrum measurements, both configurations are situated between electrodes with dissolved hydrogen. With the aid of previous theoretical calculations [16,17] for the platinum-hydrogen system and the comprehensive knowledge of the electron structure of bulk palladium hydride [18], reasonable microscopic pictures can be suggested for these configurations, which is discussed below.

In hydrogen embedded platinum junctions a single new configuration appears, which corresponds to a bridge of a H_2 molecule between the platinum electrodes [4] [for an illustration, see Fig. 4(a)]. This configuration has a single channel with perfect transmission as proven by conductance fluctuation measurements. The interpretation of this result is supported by theoretical calculations for an arrangement where the hydrogen molecule lies parallel to the contact axis [16]. Though this configuration is expected to have a single channel, the perfect transmission is surprising. The high conductance of H_2 can be understood only from the strong hybridization between the electron states of H_2 and the d band of the electrodes. According to Ref. [16], the same conductance should be observed for a hydrogen molecule between palladium electrodes. Our measurements, however, show that the electrodes cannot be treated as pure palladium; the dissolved hydrogen has to be taken into account as well. As shown in Ref. [18], due to the presence of H atoms in the Pd host the Fermi energy is shifted upward relative to the d band of Pd. Since in pure Pd the d band is almost completely filled, the density of states (DOS) drastically decreases with an increasing amount of dissolved hydrogen. At high H concentration ($\sim 70\%$), the d band becomes completely closed, and the remaining DOS from the s band is only $\sim 20\%$ of the original one. On the basis of the demonstrative model of Ref. [16], the high DOS at the Fermi energy due to the d electrons is the reason for the large transmission through the H_2 molecule; thus, the same configuration between palladium-hydride electrodes should have a considerably smaller transmission.

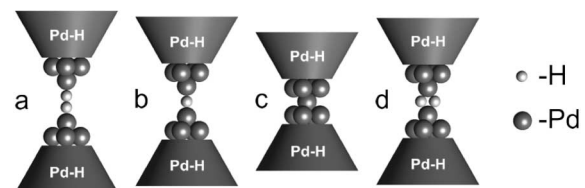


FIG. 4. Possible realizations of the new hydrogen related atomic configurations.

A quantitative estimation of the transmission can be given, assuming that the dissolved hydrogen changes only the DOS of the electrodes. We have performed a calculation with the demonstrative model of Heurich *et al.* [16] applying the DOS of PdH_x [18] instead of Pt. Inserting a reasonable concentration of $x = 0.5$ [19], the model yields a conductance of $G = 0.6G_0$.

The above argumentation implies that the configuration with $G \sim 1G_0$ is not a hydrogen bridge [Fig. 4(a)], like the one in the platinum-hydrogen system. This is strongly supported by our conductance fluctuation measurements as well, which show that the configuration at $1G_0$ has more than one open conductance channel, whereas the H₂ bridge should have a single channel. On the other hand, the hydrogen bridge is a reasonable candidate for explaining the second configuration with $G \sim 0.5G_0$. The estimated conductance value of the H₂ bridge is in good agreement with the $\sim 0.5G_0$ value, and the uncertainty of the peak position can be explained by the changes in the amount of dissolved hydrogen.

We note that in the platinum-hydrogen system the vibrational spectrum measurements with H₂, D₂, and HD molecules provided the conclusion that the new configuration is a molecular and not an atomic bridge. The same study on Pd contacts is hindered by two reasons. Because of the unsuppressed conductance fluctuations, the nonlinearity of the I - V curves in atomic-sized contacts is strongly dominated by quantum interference structures, and the vibrational spectrum is hardly detectable. Furthermore, the vibrational modes of a molecular bridge are positioned in the same energy region as those of the dissolved atoms; thus, the separation of the two features is problematic. Therefore we believe that the configuration with $G \sim 0.5G_0$ can be a molecular as well as an atomic hydrogen bridge between palladium-hydride electrodes [Figs. 4(a) and 4(b), respectively].

For the configuration with $G \sim 1G_0$, we propose two atomic configurations. The first one is a single-atom Pd junction between Pd-H electrodes [Fig. 4(c)]. The conductance of $1.8G_0$ for the same configuration between pure electrodes is shifted close to 1 quantum unit due to the dissolution of hydrogen in the electrodes. This reduction of the conductance is reasonable considering the 30%–60% decrease of the DOS at the Fermi energy [18]. This arrangement may have up to five open channels, which agrees with the unsuppressed conductance fluctuation. A second possibility is the Pd₂H₂ complex similar to what was recently proposed for platinum junctions [17] [Fig. 4(d)]. In platinum this arrangement is found to have three open channels with a total conductance of $1G_0$. From these two candidates the monoatomic Pd contact is supported by the observation that at high hydrogen concentration the configuration with $G \sim 1G_0$ disappears.

In conclusion, we have experimentally investigated the influence of adsorbed hydrogen on the behavior of atomic-sized palladium junctions. We have found that the adsorption of hydrogen completely reshapes the conductance

histogram: The original peak of a monoatomic Pd contact disappears, and two new hydrogen-related peaks emerge at $G \sim 1G_0$ and $G \sim 0.5G_0$. Our phonon spectrum measurements have shown that these configurations are situated between electrodes containing dissolved hydrogen atoms. The dissolution of hydrogen makes a crucial difference compared to platinum nanocontacts, where the hydrogen is found only on the surface. Combining the recent results on Pt-H₂ junctions and the consequences of the dissolution of hydrogen on the band structure of the Pd electrodes, we have proposed possible explanations for the new peaks in the histogram.

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