Interaction of hydrogen molecules with superconducting nanojunctions

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In this paper the interaction of hydrogen molecules with atomic-sized superconducting nanojunctions is studied. It is demonstrated by conductance histogram measurements that the superconductors niobium, tantalum and aluminum show a strong interaction with hydrogen, whereas for lead a slight interaction is observed, and for tin and indium no significant interaction is detectable. For Nb, Ta and Pb subgap method is applied to determine the transmission eigenvalues of the nanojunctions in hydrogen environment. It is shown, that in Nb and Ta the mechanical behavior of the junction is spectacularly influenced by hydrogen reflected by extremely long conductance traces, but the electronic properties based on the transmission eigenvalues are similar to those of pure junctions. Evidences for the formation of a single-molecule bridge between the electrodes – like in recently studied platinum hydrogen system – were not found.

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I. INTRODUCTION

The future aim of building functional single-molecule electronic devices necessitates the development of reliable characterization techniques of molecular nanojunctions. In many cases the direct microscopic imaging of the junction is not possible, thus all the information about the molecular device must be extracted from its electronic properties. The conduction properties of the device can be characterized by the so-called mesoscopic PIN-code – the set of the transmission eigenvalues of the junction. According to the Landauer formula, the linear conductance of the junction is proportional to the sum of the transmission eigenvalues, \( G = 2e^2/h \sum \tau_i \), where \( G_0 = 2e^2/h \) is the quantum conductance unit. For the determination of the individual transmission eigenvalues the measurement of further quantities is required. Conductance fluctuation and shot noise measurements provide an additional independent combination of the mesoscopic PIN code, respectively \( \sum \tau_i(1 - \tau_i^2) \) and \( \sum \tau_i(1 - \tau_i) \) can be determined. These methods were successfully applied to show that a molecular hydrogen junction between platinum electrodes has a single, perfectly transmitting channel. However, for a junction with arbitrary conductance and a larger number of conductance channels the conductance fluctuation and shot noise measurements are not efficient.

By placing the junction between superconducting electrodes, and measuring the nonlinear subgap features in the current voltage characteristic, principally all the transmission eigenvalues can be determined. This method was successfully used in the study of single-atom junctions of Nb, Pb and Al, demonstrating that even for a junction with 5–6 conductance channels the transmission eigenvalues can be determined with high precision. With the use of proximity effect the sub-gap method can even be extended for non-superconducting materials, as shown by the sub-gap measurements on gold nanojunction. According to our knowledge, studies on molecular nanojunctions applying the superconducting subgap method were not yet reported.

Beside the study of the mesoscopic PIN-code and the corresponding elastic transmission properties of the junction, a fingerprint of the inelastic excitations of the molecular device can be given by point-contact spectroscopy and inelastic electron tunneling spectroscopy measurements. The excitation of the vibrational modes of the molecular device or the excitation of the molecule to an other configurations with different binding energy are reflected by step- or even peak-like structures in the differential conductance, \( dI/dV(V) \) characteristics. As the subgap features appear below the superconducting gap on the millivolt or even sub-mV scale, whereas the inelastic excitations are typically observed in the range of 30–100 mV, from a single \( I-V \) curve measurement on a molecular junction between superconducting electrodes not only the mesoscopic PIN-code can be determined, but also the inelastic excitations can be studied.

In this paper we study the behavior of superconducting atomic-sized nanojunctions in interaction with the simplest molecule, hydrogen. As superconducting electrodes Nb, Ta, Al, Pb, Sn, and In samples were used. For all these materials the interaction is investigated by the conductance histogram technique, and for the superconductors Nb, Ta and Pb the subgap curves of the molecular nanojunctions are also studied. The \( I-V \) characteristics of the molecular junctions show clear-cut subgap features, from which the transmission eigenvalues can be extracted with high precision.

II. EXPERIMENTAL METHOD

Our experiments were performed by the mechanically controllable break junction (MCBJ) technique at liquid helium temperature (\( T = 2.2 - 4.2 \) K). The atomic-sized nanojunctions were created under cryogenic vacuum, by breaking high-purity wires. The hydrogen molecules were
FIG. 1: Conductance histograms of Nb, Ta, Al, Pb, Sn and In junctions in high vacuum (line graphs) and in hydrogen environment (area graphs). The histograms were recorded at $T = 4.2$ K and $V = 10$ mV. All the histograms are normalized to the precise number of the included traces (4000-8000).

admitted to the sample space through a solenoid valve of a mass flow controller, from a container of high-purity hydrogen with reduced pressure ($\sim 10$ mbar). For the removal of contaminants a liquid nitrogen cold-trap was used. By applying short pulses of 100 ms on the solenoid valve, doses of $\sim 0.1 \mu$mol H$_2$ could be admitted the sample holder. The molecules were directed to the close vicinity of the junction in the cryogenic part of the setup through a capillary tube. For the reduction of the noise level the input signal was attenuated and RC filters were placed close to the junction. According to the width of the peaks in the $dI/dV(V)$ curves of Nb, Ta and Pb tunnel junctions the noise level was smaller than 80 $\mu$V.

III. CONDUCTANCE HISTOGRAMS AND INDIVIDUAL CONDUCTANCE TRACES

Figure 1 shows the conductance histograms of Nb, Ta, Al, Pb, Sn and In junctions both in high vacuum and in hydrogen environment. In pure environment the d-metals Nb and Ta and the p-metals Pb and Sn exhibit a single broad peak corresponding to single atom junctions, whereas Al shows more well-defined peaks. All these results agree with previous observations. Indium, for which former measurements are not known to us, shows a rather unique histogram: a sharp peak is observed at the conductance quantum unit and further features are seen at higher conductance values.

In hydrogen environment the histograms of Pb, Sn and In show similar shape as in high vacuum. For lead the peak becomes broader, and shows a significant shift towards higher values; tin does not show any change; whereas for indium the 1 $G_0$ peak is reproduced, and the change at higher conductance values is within the scatter of the pure histograms from sample to sample. In contrast for Nb, Ta and Al the addition of hydrogen has a very strong influence on the histograms, in every case a rather featureless distribution is observed demonstrating the appearance of a large number of different hydrogen-related configurations. In Nb frequently a small shoulder near the quantum conductance unit is superimposed on the featureless histogram. In Ta even a small peak at 1 $G_0$ can be seen after the admission of hydrogen which disappears by time, as already reported in Ref. 12. It is noted that all the hydrogen-related features disappear if the histograms are recorded at large bias voltage ($V \approx 300 - 400$ mV), as the hydrogen is desorbed due to the local heating of the junction.

As the histograms are normalized to the number of traces included, the weights in pure and hydrogen environment can be directly compared. Accordingly, at higher conductance values where the effect of hydrogen is negligible the two histograms fall onto each other. For aluminum the overall weight of the two histograms is similar, just the characteristic peaks of aluminum are smoothed out in the hydrogen affected histogram. In Nb and Ta a remarkable feature is observed: until the conductance of the pure single atom contacts ($G \approx 2.3 G_0$) the two histograms are almost the same, but below that value the pure histogram shows a minimum, whereas the in the hydrogen affected case a huge weight is observed.

FIG. 2: Typical conductance traces of Nb, Ta, and Al junctions in high vacuum (gray) and in hydrogen environment (black).

We have found, that the strong interaction of Nb, Ta, and Al with hydrogen is not only statistically detectable by conductance histograms, but it is also clearly visible on individual conductance traces. The gray curves in Fig. 2 show typical conductance traces of pure Nb, Ta, and Al, respectively. After forming a single-atom junction a sudden jump to the tunneling region is observed. In contrast the conductance traces in hydrogen environment show various different conductance values with a lot of jumps. The difference is remarkable, just by looking at a single conductance trace the presence of hydrogen
can be detected. In the case of Nb and Ta it is clearly visible that the hydrogen affected traces are significantly longer than the pure traces. Surprisingly, this kind of traces are not only observed during the rupture of the junction, but the same behavior is seen when the electrodes are pushed together. In the case of aluminum the characteristic positive slope of the plateaus is preserved in hydrogen environment, just more smaller jumps are observed instead of the few larger jumps in high vacuum. For Pb, Sn and In the characteristic shape of the individual conductance traces did not change by the addition of hydrogen, as expected.

The effect of hydrogen can be further studied by investigating the length of the conductance traces. As the plateau length histograms did not show any distinct feature (e.g. chain formation), we characterize the length of the conductance traces. As the plateau length histograms did not show any distinct feature. (b) Differential conductance in the superconducting gap region. (c) I − V curve in the superconducting gap region and the best theoretical fit corresponding to the set of channel transmissions \{0.70, 0.14, 0.08, 0.05, 0.04\}.

FIG. 3: I − V curve measurement on a hydrogen affected Nb junction with \(G \approx 1 \Omega_0\). (a) The differential conductance in a wide voltage window, showing negative differential conductance phenomenon and a large conductance noise at higher voltages. (b) Differential conductance in the superconducting gap region. (c) I − V curve in the superconducting gap region and the best theoretical fit corresponding to the set of channel transmissions \{0.70, 0.14, 0.08, 0.05, 0.04\}.

IV. SUBGAP ANALYSIS

Fig. 3 shows the results of an \(I − V\) curve measurement on a \(G = 1 \Omega_0\) Nb junction in hydrogen environment. Panel (a) shows the the differential conductance, \(dI/dV\) in a wide voltage window. The curve shows a negative differential conductance peak at \(V = 40\, \text{mV}\) and a large noise at higher voltages. Both features are characteristic of molecular nanojunctions, and cannot be seen in pure environment. The negative differential conductance peak is related to the scattering on a two-level system formed by the molecular junction, but the more precise microscopic background of the phenomenon is still debated.\(^{14,15}\) The observation of a shoulder at the quantum conductance unit in the histogram of niobium-hydrogen, together with the appearance of a peak-like structure close to the previously observed vibrational energy in Pt-H\(_2\) molecular bridges would imply the formation of a hydrogen molecular bridge between the niobium electrodes similarly to the Pt-H\(_2\) system.\(^{4,10}\) This hypothesis can be tested by zooming on the superconducting features in the middle of the \(I − V\) curve. Fig. 3 shows the differential conductance within the gap region exhibiting distinct peaks at the fractional values of the gap due to multiple Andreev reflections.\(^{4,11,10}\) Fig. 3 shows the \(I − V\) curve itself, which is fitted by the theory of multiple Andreev reflections.\(^{11,15}\) The fitting shows that the junction has 5 open channels, and the corresponding transmission probabilities are: \{0.70, 0.14, 0.08, 0.05, 0.04\}. This result clearly shows that no hydrogen molecular bridge is formed, which would have a single conductance channel. Figure 3 shows further examples of subgap curves in niobium-hydrogen junctions with \(G \approx 1 \Omega_0\). It is seen, that occasionally subgap curves with a single, perfectly transmitting conductance channel are indeed observed, but these curves were rather rare, and occasionally similar curves were also observed in pure Nb junctions. In the majority of the cases the second conductance channel also gives a significant contribution. We note, that in our measurements we did not observe clear vibrational spectra like in the Pt-H\(_2\) system,\(^{4,10}\) in hydrogen environment rather huge peak-like structures and/or large noise of the conductance at higher bias voltage were seen, which are both demonstrated in Fig. 3.

Taking advantage, that with the subgap method the complete mesoscopic PIN-code of the junction can be determined at an arbitrary point of the conductance trace, we have performed a large number of subgap measurements in a wide conductance interval of 0.1 \(\Omega_0\) - 3 \(\Omega_0\), both for pure and hydrogen affected Nb, Ta and Pb junctions. Our results show the strange conclusion, that in the whole conductance interval no statistical difference can be pointed out between the channel distribution of the pure and hydrogen affected junctions. This result is demonstrated for Ta junctions in Fig. 3. The five panels show the distribution of the transmission probabilities for a large number of independent configurations both in
FIG. 4: Subgap structure measurements on 4 different niobium junctions in hydrogen environment with $G \approx 1 G_0$. The set of transmission eigenvalues corresponding to the best fits (thin black lines) are also indicated on the figure.

FIG. 5: Transmission probabilities of a large amount of independent Ta nanojunctions in high vacuum (gray squares) and in hydrogen environment (black circles) as a function of conductance.

V. SUMMARY AND DISCUSSION OF THE RESULTS

Our measurements have shown that in Nb, Ta and Al junctions the conductance histograms are strongly reshaped due to the interaction with hydrogen; in Pb some effect of hydrogen is observed, whereas in Sn and In no significant change is observed.

In Al junctions the results imply, that hydrogen stabilizes various arrangements with slightly different conductance values, and so the histogram is smoothed and the individual traces show several small steps. The overall weight of the histogram and length of the traces does not change considerably, and the characteristic shape of the plateaus with positive slope is also preserved.

For the subgap analysis of aluminum-hydrogen junctions sub-kelvin temperatures would be required, which is not available in our setup.

In Pb junctions the subgap analysis shows that the transmission probabilities in hydrogen environment are indistinguishable from those of pure junctions. This together with the slight changes in the histogram imply that the interaction of lead with hydrogen is weak.

Niobium and tantalum junctions show a very similar behavior, which is not surprising, as Nb is placed above Ta in the periodic table. Both metals show strong interaction with hydrogen, in $H_2$ environment a rather featureless histogram is observed, in which at low conduc-

pure and hydrogen environment. It is clear that the opening of the conductance channels follow the same tendency for pure and hydrogen affected junctions, the measured points fall onto each other within the scattering of the data. The same behavior was observed for Nb and Pb junctions as well, for which the results are demonstrated in Table I showing the mean value and the standard deviation of the channel transmissions at some characteristic conductance values. For Nb these values were chosen as 0.3 $G_0$ corresponding to a point from a tail of the hydrogen affected histogram with a large weight; 1 $G_0$ corresponding to the shoulder in the hydrogen affected histogram; and 2.3 $G_0$ corresponding to the peak due to single-atom contacts in the pure histogram. For Pb the results for 1.5 $G_0$ and 2.2 $G_0$ are presented corresponding to the peak positions in the pure and hydrogen affected histograms, respectively. For comparison the results for Ta junctions with $G = 1 G_0$ corresponding to the peak in the hydrogen affected histogram are also shown. It is seen that at each conductance value the mean value of all the transmission coefficients for pure and hydrogen affected junctions are the same within the standard deviation of the data.

| $G=0.3 G_0$ | $G=1 G_0$ | $G=2.3 G_0$ |
|-------------|-----------|-------------|
| Nb  | Nb+H$_2$ | Nb  | Nb+H$_2$ | Nb  | Nb+H$_2$ |
| $t_1$ | 0.27±0.03 | 0.27±0.03 | 0.71±0.14 | 0.7±0.13 | 0.93±0.07 | 0.89±0.08 |
| $t_2$ | 0.02±0.01 | 0.02±0.01 | 0.13±0.09 | 0.17±0.09 | 0.62±0.11 | 0.55±0.09 |
| $t_3$ | 0.01±0.01 | 0.01±0.01 | 0.08±0.05 | 0.06±0.03 | 0.42±0.09 | 0.43±0.11 |
| $t_4$ | --       | --       | 0.05±0.03 | 0.04±0.03 | 0.17±0.09 | 0.22±0.10 |
| $t_5$ | --       | --       | 0.03±0.03 | 0.03±0.03 | 0.16±0.08 | 0.21±0.08 |

TABLE I: The mean value and the standard deviation of the transmission eigenvalues at some characteristic conductance values of Nb, Ta and Pb junctions both in high vacuum and in hydrogen environment. The indicated conductance values were adjusted with an accuracy of a 0.03 $G_0$, and at each conductance value the subgap curves were recorded on 30 independent junctions.
Contacts are formed. For both metals some features can be seen close to the quantum conductance unit, in Nb occasionally a shoulder is seen in the hydrogen affected histogram, whereas in Ta even a peak can grow at 1 G₀, which disappears by time. The strong interaction with hydrogen is evident from individual conductance traces, instead of the sudden jump to tunneling extremely long traces with a lot of jumps are observed. The length analysis shows that in hydrogen the average length to break a single atom contact is 6 – 9 times larger than in high vacuum. This feature indicates a completely different mechanical behavior of hydrogen affected Nb and Ta junctions. As no periodic peaks are observed in the plateaus’ length histogram, and the extremely long traces are also observed during the closing of the junctions, the formation of atomic chains is not a plausible explanation for this strange phenomenon. Rather a very soft, plastic behavior of the junction’s neighborhood and the pulling of a long neck is expected. The subgap analysis of the hydrogen affected junctions has shown that in spite of the growth of a shoulder or even a peak near the conductance quantum unit in the histograms of Nb and Ta and the frequent occurrence of peak-like structures in the differential conductance curves, the formation of a molecular hydrogen bridge with a single conductance channel is not observed in the large majority of the cases. Furthermore our results show that the mesoscopic PIN-code of the hydrogen affected junctions are the same as those of pure junctions. These results imply, that the interaction with hydrogen causes a soft, plastic behavior of the junctions, but no well-defined single-molecule contacts are formed, and the conduction properties are still dominated by Nb and Ta.

VI. CONCLUSIONS

In conclusion, we have studied the interaction of superconducting metals Nb, Ta, Al, Pb, Sn and In with hydrogen molecules. The analysis of conductance histograms and individual conductance traces shows that Nb, Ta and Al junctions strongly interact with hydrogen. We have also applied the superconducting subgap method to determine the mesoscopic PIN-code of molecular nanojunctions. Our measurements show that in Nb and Ta the interaction with hydrogen completely changes the mechanical behavior of the junctions, but the electronic properties based on the transmission probabilities are the same as those of pure junctions. These results imply, that the interaction with hydrogen causes a soft, plastic behavior of the junctions, but no well-defined single-molecule contacts are formed, and the conduction properties are still dominated by Nb and Ta.

Our measurements also demonstrate, that the break junction method with superconducting electrodes provides a powerful tool for the study of molecular nanojunctions: beside the fine tuning of the electrode separation both the elastic transmission eigenvalues of the junctions can be determined, and the inelastic excitations of the junction can be studied. All these together provide an outstanding amount of information about the studied molecular nanostructures.

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