Low-temperature hydrogen absorption into V and Nb metals from liquid hydrogen

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Abstract. We report experimental study on low-temperature hydrogen (H) absorption in vanadium (V) and niobium (Nb) nanocontacts below \( T = 20 \) K using a point-contact spectroscopy (PCS) technique. When a small bias voltage is applied between both sides of nanocontacts immersed in liquid H\(_2\), the differential conductance (\( dI/dV \)) and the second derivative (\( d^2I/dV^2 \)) are changed from those for pure V and Nb nanocontacts. Further, the spectra approach to those for a high concentrated phase of H with increasing the bias voltage. The results indicate that in-situ investigation of H absorption process from liquid H\(_2\) is possible through \( dI/dV \) and \( d^2I/dV^2 \) measurements using the PCS technique.

1. Introduction
Hydrogen (H) atoms absorbed in metals occupy interstitial sites of their host lattice, which shows strong quantum characters because of its light mass [1]. A most famous example is H diffusion via quantum tunnelling (QT). H diffusion inside metals is governed by thermal activation process at high temperature, while the diffusion due to QT becomes dominant below liquid nitrogen temperature [1]. However, it is difficult to detect QT of H experimentally. Thus most studies on QT of H are discussed in terms of the temperature dependence of the diffusion rate or the relaxation time [1,4,5]. The temperature dependence of the diffusion rate obeys the Arrhenius equation at high temperatures, while it deviates from the equation at lower temperatures due to the change of their diffusion process. These suggest that understanding of H diffusion process is not complete yet because the experimental evaluation of the diffusion rate depends on the sample quality.

We focus on point-contact spectroscopy (PCS) to investigate low-temperature properties of metallic hydrides [6]. In a nanoscale contact that size is smaller than the mean free path of conduction electrons, the electrons accelerated by a bias voltage are transported through the contact ballistically, and then lose their energy by inelastic scattering with excitations such as phonons. This leads to a nonlinear relationship between current (\( I \)) and voltage (\( V \)) character [7,8]. The existence of H atom affects the electron transport, enabling to explore the properties of hydrides by tracing \( dI/dV \) and \( d^2I/dV^2 \) spectra using differential conductance measurements [6,9].

In addition, we found that PCS experiments advance H absorption in palladium (Pd) nanocontacts even below \( T = 20 \) K. When a small bias voltage is applied between the nanocontacts immersed in liquid
H₂, the $d/dV$ and $d^2I/dV^2$ spectra show the time evolution from the pure Pd to the Pd hydride, indicating that a large amount of H atoms go into Pd [6]. The results suggest the following absorption process. First, H₂ molecules dissociate into atoms at the surface of Pd due to steering effect [10]. Note that the dissociation occurs without the activation energy in Pd according to the theoretical calculation [11]. Then, H atoms are absorbed in Pd via QT by applying the bias voltage because the thermal hopping process of H is prohibited at $T = 20$ K [6].

In this study, to investigate the low-temperature H absorption in different metals other than Pd, we have performed PCS experiments in vanadium (V) and niobium (Nb) nanocontacts, which are known as H absorption metals, immersed in liquid H₂. H absorption are confirmed for $T < 20$ K as in the case of Pd nanocontacts. The results suggest that applying a bias voltage between nanocontacts advances H absorption due to QT. Further, this method would be a powerful tool for exploring QT of H.

2. Experimental

The present experiments are carried out with a home-made cryostat attaching a MCBJ apparatus. Nanocontacts are made in vacuum and low-temperature environment to prevent surface contamination and oxidation. V and Nb polycrystalline wire (99.8 % and 99.9 % respectively, 0.25 mm diameter) were used for samples. Hydride samples, V₁₉H₆ and NbH₀.₅₂, are prepared by loading H atoms into these wires at high temperatures with the gas absorption method [12]. The H contents are determined in accordance with each pressure-temperature phase diagram of V-H and Nb-H system. In MCBJ experiments, sample wires on a phosphor-bronze substrate are stretched by bending the substrate with mechanical force, which is applied by a screw and a piezo element as shown in figure 1. The size of nanocontacts is changed continuously from atomic scale to micrometres and is kept over several hours by avoiding thermal input to the sample space [13, 14]. The MCBJ apparatus is mounted in an inner cell with flexible bellows inside the vacuum chamber to immerse the nanocontacts in liquid H₂ [15]. It is worthy to note that the electrical conductivity measurements are performed in liquid H₂, preventing the temperature increase due to Joule heating in the nanocontacts.

The differential conductance $dI/dV$ spectra and the second derivative $d^2I/dV^2$ are measured as a function of bias voltage using a lock-in technique with 1 kHz modulation [7]. $dI/dV$ and $d^2I/dV^2$ are proportional to the first and second harmonics of the modulation frequency, respectively, so that the two spectra are measured simultaneously using two lock-in amplifiers.

3. Results

We show $d/dV$ and $d^2I/dV^2$ spectra for a pure V nanocontact measured in vacuum at $T \sim 15$ K in figures 2(a) and 2(b), respectively. Here, the vertical axis is plotted in the universal conductance unit $G_0=2e^2/h$. In pure V nanocontacts, the intensity of $d/dV$ spectra is lowered rapidly with increasing the bias voltage, which is caused by backscattering between the conduction electrons and phonon excitations [7]. $d^2I/dV^2$ spectra correspond to the density of states for phonon excitation exhibit a sharp peak at $|V| \sim 20$ mV, which is consistent with the previous experiments [16,17].

The bias voltage dependence of the spectra is significantly modified by the existence of H atoms as shown in figures 2(a) and 2(b). The width of the $d/dV$ spectrum is broadened. Besides, the peak at $|V| \sim 20$ mV in the $d^2I/dV^2$ spectrum is strongly suppressed. These features can be understood by the change of the transport character in the nanocontacts from ballistic to diffusive regime by hydrogenation [18,
In hydride sample H atoms occupy interstitial lattice sites, causing the strain fields at around H atoms. This reduces the mean free path of conduction electrons.

The similar features are observed in pure Nb and NbH$_{0.43}$ nanocontacts as shown in figures 3(a) and 3(b). The width of the $dI/dV$ spectrum is broadened by hydrogenation. A sharp peak at $|V|$ ~ 15 mV in the $d^2I/dV^2$ spectrum of pure Nb is strongly suppressed. These results demonstrate that hydrogenation causes substantial change for $dI/dV$ and $d^2I/dV^2$ spectra because of scatterings between H atoms and conduction electrons, which enables to trace H absorption and diffusion process using the PCS technique as in the case of Pd.

Next we describe the results on low-temperature H absorption experiments in V and Nb nanocontacts. The procedure is done as follows. V and Nb nanocontacts are prepared at $T$ ~ 15 K in vacuum by MCBJ method, and then liquid H$_2$ is introduced into the inner cell of the cryostat. After immersing the nanocontacts in liquid H$_2$, we start the measurements. $dI/dV$ and $d^2I/dV^2$ spectra are measured at the bias voltage of $V_m = 20$ mV, 30 mV, 40 mV, 60 mV and 80 mV, where $V_m$ is increased monotonously. During the measurements, the zero bias conductance $G(0)$, which is obtained from $dI/dV$ at 0 mV, are kept to be 800 $G_0$ with feedback adjustment.

Figures 4(a) and 4(b) plot the bias voltage dependence for $dI/dV$ and $d^2I/dV^2$ spectra in V nanocontacts, respectively. After starting the measurements in liquid H$_2$ by applying $V_m = 20$ mV, $dI/dV$ and $d^2I/dV^2$ spectra have been already changed from those for the pure nanocontact. On the other hand, the spectra show no change as long as the bias voltage is kept at $V_m = 20$ mV. This indicates that H absorption is finished immediately after starting the measurements. When $V_m$ is increased to 30 mV, $dI/dV$ spectra are further broadened and the intensity of $d^2I/dV^2$ is decreased. The broadening of $dI/dV$ spectra is progressed with increasing $V_m$. It is easily seen that $dI/dV$ spectra approach to those for VH$_{0.43}$.
in figures 2(a), indicating that H absorption is developed by applying the bias voltage. It takes about 30 min for the complete change after increasing \( V_m \), which is much faster than that of Pd nanocontacts with more than 10 hours [6]. In Nb nanocontacts, qualitatively the same features are observed as shown in figures 5(a) and 5(b).

From these results, we conclude that H absorption is developed in V and Nb nanocontacts even below \( T = 20 \) K, and propose the following scenario for the low-temperature H absorption. First, H\(_2\) molecules dissociate into atoms at the surfaces of V and Nb nanocontacts. It is well known that the activation energy for the dissociation is lowered not only by the high reactivity at the surface of transition metals, but also by the lattice distortions and defects, which are inevitable for the nanocontacts fabricated by MCBJ method. As a result, the kinetic energy of some H\(_2\) molecules, which have a large energy distribution due to quantum effect [20], surpasses the activation energy, leading to the dissociation even at \( T = 15 \) K. Then, H atoms are absorbed when a small bias voltage is applied between the nanocontacts.

![Figure 4](image1.png)

**Figure 4.** (Color online) The bias voltage dependence of (a) \( dI/dV \) and (b) \( d^2I/dV^2 \) spectra in V nanocontacts immersed in liquid H\(_2\). The spectra in (a) and (b) are measured for the bias amplitude at \( V_m = 20, 30, 40, 60, 80 \) mV, after finishing the spectra changes by H absorption into the nanocontacts. For comparison, the spectra for pure nanocontact (dashed line) are plotted in the figures. The \( d^2I/dV^2 \) curve is scaled down one-half.

![Figure 5](image2.png)

**Figure 5.** (Color online) The bias voltage dependence of (a) \( dI/dV \) and (b) \( d^2I/dV^2 \) spectra in Nb nanocontacts immersed in liquid H\(_2\). The spectra in (a) and (b) are measured for the bias amplitude at \( V_m = 20, 30, 40, 60, 80 \) mV, after finishing the spectra changes by H absorption into the nanocontacts. For comparison, the spectra for pure nanocontact (dashed line) are plotted in the figures. The \( d^2I/dV^2 \) curve is scaled down one-half.

Additionally, it is important that the evolution can be traced using the PCS technique. From the fact that the thermal hopping process is frozen at \( T = 20 \) K, it is reasonable to consider that H absorption is caused by the phonon assisted tunnelling process which is excited by an inelastic scattering with the accelerated electrons [1]. Moreover, time for the complete change of the spectra in V and Nb experiments is much faster than that in the Pd nanocontacts. This difference is likely caused by the
difference of crystal structure in the base metal. The wave function of H atom in bcc metals such as V and Nb is more extended than that in fcc metal of Pd [21], which increases the probability of H diffusion. At $V_m = 80 \text{ mV}$, a broad peak is seen at around $V = 30 \text{ mV}$, which is apparently higher than $V = 15 \sim 20 \text{ mV}$ in pure V and Nb nanocontacts. The increase of Debye temperature due to hydrogenation can be responsible for this shift. It was revealed that the Debye temperatures of VH$_x$ and NbH$_x$ are raised with the H contents [22]. This implies that the mean value of the phonon density of states should move to higher energy side by H absorption, resulting in the shift of the peaks in $d^2I/dV^2$ spectra.

Surprisingly, the intensity of $d^2I/dV^2$ spectra grows with increasing $V_m$ from 40 mV to 80 mV in the both nanocontacts. Generally, H absorption shortens the electron mean free path, reducing the intensity of $d^2I/dV^2$ spectra as mentioned above. Therefore, the growth suggests the increase of electron mean free path. This would be caused by the structural transition of H arrangement from $\alpha$ phase with a random occupation of the interstitial sites to $\beta$ phase with the periodic arrangement with increasing H contents. Actually, a resistivity drop is observed at the boundary between $\alpha$ phase to $\beta$ phase in bulk V [23, 24], implying the increase of the electron mean free path in $\beta$ phase. Recalling that $\beta$ phase appears H concentration higher than 0.5, we could perform in-situ investigation of the H absorption process via QT for a wide range of H concentration through $dI/dV$ and $d^2I/dV^2$ measurements using PCS.

4. Conclusion

We have performed H absorption experiments in vanadium (V) and niobium (Nb) nanocontacts using the PCS technique. The $dI/dV$ and $d^2I/dV^2$ spectra in hydride nanocontacts prepared by the gas absorption method are clearly different from those in the pure nanocontacts, indicating that PCS is used for tracing the H absorption and diffusion process in metals. When a small bias voltage is applied between the nanocontacts immersed in liquid H$_2$, the spectra shape is changed with increasing the bias voltage, demonstrating that H absorption into the nanocontacts is developed even below $T = 20 \text{ K}$. Since the thermal hopping of H is frozen at $T = 20 \text{ K}$, this should be explained by QT. Time for the complete change of the spectra in V and Nb experiments is much faster than that in the Pd nanocontacts, which is probably understood by the difference of crystal structure in the base metal. The bias voltage dependence of $d^2I/dV^2$ spectra implies that a high concentrated phase of H is realized by applying a high bias voltage between the nanocontacts. These results suggest that in-situ investigation of H absorption process via QT is possible through $dI/dV$ and $d^2I/dV^2$ measurements using PCS.

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References

[1] Fukai Y 2005 *The Metal-Hydrogen System*, 2nd Edition (Springer, Berlin)
[2] Nelin G and Scöld K 1975 *J. Phys. Chem. Solids* 36 1175
[3] Arons R R, Bohn H G and Lütgemeier H 1974 *Solid State Commun.* 14 1203
[4] Minissale M, Congiu E, Baouche S, Chaabouni H, Moudens A, Dulieu F, Accolla M, Cazaux S, Manico G and Pirronello V 2013 *Phys. Rev. Lett.* 111 053201
[5] Shannon R J, Blitz M A, Goddard A and Heard D E 2013 *Nature Chem.* 5 745
[6] Ienaga K, Takata H, Onishi Y, Inagaki Y, Tsuji H, Kimura T and Kawae T 2015 *Appl. Phys. Lett.* 106 021605
[7] Naidyuk Yu G and Yanson I K 2004 *Point-Contact Spectroscopy* (Springer, Berlin)
[8] Jansen A G M, Mueller F M and Wyder P 1977 *Phys. Rev. B* 16 1325
[9] Csonka Sz, Halbritter A, Mihály G, Shkil'yar'evskii O I, Speller S and van Kempen H 2004 *Phys. Rev. Lett.* 93 016802
[10] Gross A, Wilke S and Scheffler M 1995 *Phys. Rev. Lett.* 75 2718
[11] Wilke S and Scheffler M 1996 *Phys. Rev. B* 53 4926
[12] Veleckis E and Edwards R K 1969 *J. Phys. Chem* 73 683
[13] Ienaga K, Nakashima N, Inagaki Y, Tsujii H, Honda S, Kimura T and Kawae T 2012 *Phys. Rev. B* 86 064404 (2012).
[14] Ienaga K, Nakashima N, Inagaki Y, Tsujii H, Kimura T and Kawae T 2012 *Appl. Phys. Lett.* 101 123114
[15] Ienaga K, Yokota T, Nakashima N, Inagaki Y, Tsujii H and Kawae T 2012 *J. Phys.: Conf. Ser.* 400 042019
[16] Rybaltchenko L F, Yanson I K and Fisun V V 1980 *Sov. Phys.-Solid State* 22 1182
[17] Yanson I K, Bobrov N L, Rybaltchenko L F and Fisun V V 1983 *Sov. J. Low Temp. Phys.* 9 596
[18] Yanson I K, Kulik I O and Batrak A G 1981 *J. Low Temp. Phys.* 42 527
[19] Lysykh A A, Yanson I K, Shklyarevski O I and Nayduyk Yu G 1980 *Solid State Commun.* 35 987
[20] Boninsegni M 2009 *Phys. Rev. B* 79 174203
[21] Sugimoto H and Fukai Y 1980 *Phys. Rev. B* 22 670
[22] Ohlendorf D and Wicke E 1979 *Phys. Chem. Solids* 40 721
[23] V Westlake D G, Ockers S T and Gray W R 1970 *Metall. Trans.* 1 1361
[24] V Smith J F and Peterson D T 1982 *Bulletin of Alloy Phase Diagrams* 3 55