Impurity effects of hydrogen and deuterium in vanadium nanoconstrictions

M S Islam\textsuperscript{1,2}, Y Ueno\textsuperscript{1}, H Takata\textsuperscript{1}, Y Inagaki\textsuperscript{1}, K Hashizume\textsuperscript{3} and T Kawae\textsuperscript{1}

\textsuperscript{1}Department of Applied Quantum Physics, Kyushu University, Fukuoka 819-0395, Japan
\textsuperscript{2}Department of Physics, Rajshahi University, Rajshahi 6205, Bangladesh
\textsuperscript{3}Department of Advanced Energy Science and Engineering, Kyushu University, Fukuoka 816-8580, Japan

Abstract. To study non-magnetic and magnetic impurity effects at the superconductor-normal metal interfaces, we have measured the differential conductance $dI/dV$ for Josephson contacts made by vanadium (V) nanoconstrictions with a different amount of hydrogen (H) and deuterium (D) impurities, which are prepared by a mechanically controllable break junction (MCBJ) technique at low temperature. Below the superconducting transition temperature $T_C$, we have found distinct peaks within and outside the gap, known as the sub-gap structure and an over-the-gap structure respectively, due to 5\% concentration of atomic H and D on V nanocontact. Moreover, the temperature dependence of $dI/dV$ spectra represents that both structures are survived until the critical temperature $T_C$, which is consistent with the prediction of BCS energy gap. On the other hand, a very high concentrating phase (30\% atom\%) behaves as a normal metal.

Keywords: MCBJ, impurity effects, sub-gap structure and over-the-gap structure

1. Introduction

Hydrogen (H) is an ideal replacement for synthetic fuel because of its lightest weight, high abundance, high energy density and environmental cleanness of the oxidation product. Hence, understanding the role of H atoms in metals is a matter of much technological importance as well as scientific interest. Many hydrides drastically differ from their parent metals in terms of crystal structure, electronic structure and mechanical properties. Recently, superconductivity with the transition temperature $T_C$ over 200 K has been discovered in $\text{H}_2\text{S}$ [1], which would pave the way for a room temperature superconductor. To study the interaction between electrons and phonon vibrations assisted by H atoms from microscopic view points, we have investigated impurity effects of H and deuterium (D) in vanadium (V) nanoconstrictions and measured the differential conductance $dI/dV$ spectra for Josephson contacts.

Group-V metals show superconductivity, which is other interesting aspect of this series of metals. The study of impurity doping on the superconductor is one of the most significant tools for understanding the nature of electronic properties of host metals. The main purpose of this article is to examine the influence of H and deuterium (D) on the electronic properties of vanadium to obtain information about the effects of interstitial H and D on the host metal at low temperature. Since the mass difference between H and D atoms provides the highest possible mass ratios for all elements, the

\textsuperscript{1,2} Md. Saiful Islam (Email: sislamru@gmail.com)
superconducting properties could be affected by a significant modification of electron-phonon interaction. In addition, according to the net spin of the atom, D as an isotope of H, shows half-integer spin like fermion due to its constituent particles of neutron ($I = 1/2$). H atoms are generally absorbed to be almost neutral condition in metals. Therefore, the difference of neutron spin between H and D would lead to significant changes for the pair-breaking on scattering between conduction electrons and their impurities, implying the possibility to obtain a different qualitative behavior by the effect of neutron spin on superconductivity.

In the present work, we investigate the microscopic properties of metallic vanadium (V) containing several concentration of atomic H and D with the reduced dimensionality. When the material is being constricted, the electronic interactions slightly differ from those in the bulk. We measure electrical conductance of pure V constrictions down to ~ 2 K and what behaves actually does after doping a different amount of H and D on it. The differential conductance spectra show distinct peaks not only inside the superconducting gap, but also outside the gap below the superconducting transition temperature. The temperature dependence of $dI/dV$ spectra suggests that the outside peaks are related to the superconducting transition although the peaks appear at higher energies than the superconducting gap.

2. Sample Preparation

H atoms are loaded in the polycrystalline sample wire of V, which has a typical diameter of 0.25 mm with a purity of 99.8% consisting 200 ppm of Fe and 10 ppm of Mn impurities and other nonmagnetic impurities such as 1000 ppm of Cu and 500 ppm of Si, by the following procedure. By dissociating H$_2$ molecules into atoms while getting dissolved in metals, the hydrogenated and deuterated samples are prepared by a gas absorption method [2]. The H content was quantified in accordance with the pressure–temperature phase diagram of V-H and V-D.

Then, the hydrogenated and deuterated sample wires were intimately fixed on the top of the flexible phosphor-bronze substrate after making notch at the center by a commercial blade under a microscope and mounted in a triple point bending configuration in a vacuum chamber. After cooling at liquid helium temperature, the sample wire was stretched by bending the substrate mechanically. The nanocontact was made by employing a homemade MCBJ apparatus [3,4]. Due to the application of bias voltage, a piezo element was then used to control the constriction size (a few 100 nm ~ atomic-sized) precisely. Thereafter, we have measured the spectra of differential conductance $dI/dV$ as a function of the bias voltage using a lock-in technique with a frequency of 1 kHz and performed the whole experiment at cryogenic environment to keep a stable contact long time. Moreover, the cryogenic environment diminishes the thermal fluctuation and also prevents any contaminants at the contact.

3. Results and Analysis

First, we have measured the temperature dependence of resistance in pure V constrictions by using LR700 AC resistance bridge (Linear Research Inc) [5]. The resistance starts to decrease at around 5.7 K, which is consistent with the superconducting transition temperature of V, and shows almost the zero resistivity at around 3 K as illustrated in figure 1. The essence of this measurement is to observe the nature of superconductivity after the material becomes nano-sized. The differential conductance for pure V nanoconstrictions recorded as a function of bias voltage at 2 K as depicted in figure 2. A huge conductance peak at zero bias is caused by the Josephson current flowing through the identical V electrodes, as confirmed by the corresponding $I$-$V$ characteristics shown in the inset. In figure 2, the conductance enhancements indicated by the black arrows in $dI/dV$ spectrum, referred as sub-gap structure (SGS), appear at voltages $2\Delta/e$ (~ 1.7 mV), $\Delta/e$ (~ 1.1 mV) and $2\Delta/3e$ (~ 0.7 mV). These SGS peaks can be explained in terms of the first, second and third order multiple Andreev reflection
(MAR) at SN interfaces of this SNS junction that was successfully discussed in OBTK model by M Octavio et al. [6]. However, the Δ gap value is not exactly half of the 2Δ gap. In this case, the slight increase of Δ gap may be due to the effect of geometrical instability of the contact giving rise to a mismatch of the quasiparticle wavefunction at the SN interface, because the contact is prepared by MCBJ technique. Similar inconsistencies found in some superconductor-normal metal (SN), superconductor-semiconductor interfaces [7-10].

After introducing a small proportion of atomic H and D on V nanoconstrictions, we measure the differential conductance to study their impurity effects. We show the temperature dependence of resistance for VH0.05 and VD0.05 in figure 3. In comparison with pure vanadium, the isotope effects in the resistivity are not so prominent for starting transition in R-T curves but the difference of the decrease trend of resistance shows the effect of atomic concentration of H and D in vanadium. Similar findings have been mentioned by Maier et al. [11]. In case of VH0.05 and VD0.05 constrictions with a contact size of about 9 nm, we present the spectra of dI/dV in figure 4. The conductance anomaly inside the superconducting energy gap 2Δ/𝑒 indicated by the dashed line, as can be obtained from the R ~ T curves, is largely modified in both of the systems. Additionally, the corresponding Josephson currents in these nanosystems shown in the inset are affected especially at finite voltages by that amount of H and D impurities.

It is worthy to note that a series of peaks indicated by the black arrows appear outside the superconducting energy gap of 2Δ/𝑒, referred as an over-the-gap structure (OGS), by introducing H and D impurities as in figure 4. On the other hand, the peak-shape anomalies due to SGS inside the gap are blurred, suggesting that the MAR is suppressed by H and D impurities. Although the anomalies due to OGS are clearly seen in the both systems, the bias voltage at the OGS in VH0.05 is larger than that in VD0.05. Similar anomalies mentioned experimentally in both the symmetric and asymmetric niobium (Nb) dimer contacts [12]. Moreover, the conductance spectra exhibits sharp anomalies at energies larger than the superconducting energy gap in various combinations between normal metals and low- and high-Tc superconductors by a point contact Andreev reflection process [13-15]. Although a detailed satisfactory explanation of the origin of these dips is still lacking but they proposed the possible origin of such anomalies are the proximity effect [16] and the intergrain Josephson tunneling [17] for a contact made with a conventional s-wave superconductor.
Figure 3. (Color online) The temperature dependence of the resistance for vanadium nanocontact with a five percent of atomic concentration of hydrogen and deuterium.

Figure 4. (Color online) The spectra of $dI/dV$ measured for 5% of atomic H and D in V constrictions. Both spectra show the SGS and OGS features and the clear observation of OGS's indicated by the arrows. Inset: $I-V$ characteristics of the corresponding contacts.

Figure 5. (Color online) Representative spectra of $dI/dV$ as a function of bias voltage for (a) $\text{VH}_{0.05}$ and (b) $\text{VD}_{0.05}$ depending on the temperature below $T_C$. Insets: the temperature dependence of the corresponding energy gap is fitted by the BCS gap function indicated by the solid red line.

To identify the origin of OGS's, the most authentic way is to measure their temperature dependence. The temperature dependence of $dI/dV$ spectra for $\text{VH}_{0.05}$ and $\text{VD}_{0.05}$ have been presented in figures 5 (a) and (b), respectively. Obviously, the positions at all anomalies due to OGS shift to lower bias voltages with increasing temperature in the both systems. Finally, the structures disappear when the temperature is increased above $T_C$. The corresponding normalized gap energies for the last OGS peak, shown in the insets, exactly follow the phenomenological approximate closed form of the expected BCS gap function near $T = 0$ and $= T_C$ as indicated by the solid red lines [18]. According to Marchenkov et al., the position of OGS peaks in Nb dimer nanocontact is independent of temperature but only the peak amplitudes reduce with temperature until $T_C$. They also proposed that such feature can be explained by the coupling resonance between the oscillating current and the dimer vibrational modes in both the symmetric and asymmetric contacts because of considering ac Josephson effect [12]. In our measurement, however, we only observed an over gap structure in $\text{VH}_{0.05}$ & $\text{VD}_{0.05}$ but not in pure vanadium, where the normal resistance of those contacts was at around 13 $\Omega$. When the contact
resistance is increased about 5 times (~ 65 Ω), the outside anomalies are only 2 times shifted at higher voltages. Moreover, the observed anomalies in $V_{H0.05}$ & $V_{D0.05}$ cannot be explained by the multiple Andreev reflection because those peaks are clearly inconsistent with the ratio $2\Delta/en$, where $n = 1, 2, 3$. In this context, we conclude that the OGS features for VH and VD nanosystems are due to the modification of quasiparticle excitation at finite voltages with a small proportion of H and D atoms. Although the observed gap energies are $2\Delta/eV_{H}(T = 1.9 K) = 5.6$ mV for VH and $2\Delta/eV_{D}(T = 1.5 K) = 3.1$ mV for VD nanosystems but the superconducting transition at 5.4 K, is almost similar for the both systems. The difference of modified gap energies for VH and VD system may be related to the effect of mass difference and spin interaction in vanadium metal.

When 30 percent of H and D are introduced in V nanoconstrictions, the $dI/dV$ spectra have been reported in figure 6. The $I-V$ character plotted in the inset shows that the both of the materials ($V_{H0.3}$ and $V_{D0.3}$) behave as a normal metal. Namely, such concentration completely destroys the superconductivity. From the X-ray diffraction study in VD system by Hardcastle et al. [19], a body-centered cubic (bcc) phase exists until 10% of atomic concentration of H and D dissolved into vanadium metal lattice but when the concentration increases from 10%, the structure is completely changed.

![Figure 6](image)

**Figure 6.** (Color online) The observed $dI/dV$ spectra for 30 percent of atomic concentration of H and D in V nanoconstrictions exhibit normal metallic behavior even at 2 K.

4. Conclusion

We have measured the differential conductance $dI/dV$ for Josephson contacts made by V nanoconstrictions with a different amount of H and D impurities. Below the superconducting transition temperature $T_c$, distinct peaks are observed within and outside the gap due to a small amount of H and D doping on V nanocontact. Moreover, the temperature dependence of $dI/dV$ spectra represents that both structures are survived until the critical temperature $T_c$, which is consistent with BCS energy gap. On the other hand, a very high concentrating phase (30 atom%) behaves as a normal metallic state.

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