Diffusivity of Hydrogen in Tantalum between 15 and 30 K

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The diffusivity of hydrogen in tantalum was measured by means of the perturbed-angular-correlation technique. The method makes use of the radioactive decay of [181]Hf to [181]Ta and the possibility of the trapping of hydrogen at an impurity and the release of it after the nuclear conversion.

Hydrogen diffusion in tantalum[1,2] is not known below approximately 100 K although a rather high diffusivity is expected from an extrapolation of the known data. The reason for this is that the solubility of hydrogen in the α phase becomes so small at low temperatures that diffusion measurements with classical methods are impossible. The low-temperature diffusion is very interesting from a theoretical point of view because quantum mechanical effects are expected to become important.[3,4]

Hanada[5] and Engelhard[6] tried to overcome the solubility problem by quenching a hydrogen-loaded Ta sample in liquid helium. They found recovery steps in the electrical resistivity which they attributed to the mobilization of hydrogen and diffusion to precipitates. However, these experiments are extremely sensitive to impurities or small inhomogeneities which can mask the intrinsic diffusion completely. Hanada found indeed several smaller recovery steps[6,7] below the main recovery between 20 and 40 K. This makes it difficult to decide which recovery step is due to intrinsic diffusion.

In the present experiment we used the special features of a radioactive decay to attack this problem. The main idea is to trap hydrogen at the impurity [181]Hf and to release it after the nuclear decay to the matrix atom [181]Ta. The jump frequency of the released hydrogen atom can be measured directly by the perturbed angular correlation (PAC) at the same nucleus.

A description of the PAC method in connection with the present application is given by Weidinger.[8] An important point is that [181]Hf decays first to an excited state of [181]Ta which has a mean lifetime of 25.7 μs. The subsequent γ-γ cascade in [181]Ta will record whether the hydrogen atom moved away during the lifetime of this state or remained at its position. Thereby it is assumed that the radioactive decay does not influence the diffusion behavior. This is justified since the recoil energy from the β decay ($\leqslant 1.7$ eV) is far below the threshold for a displacement of the atom, and electronic defects and vibrational excitations disappear in metals in a very short time ($< 10^{-10}$ s). In addition, a static hydrogen configuration is observed at low temperatures and it is only the change of this configuration which enters the analysis.

The samples (ca. 50 mg) were prepared by melting high-purity Ta in UHV ($\leqslant 10^{-7}$ Pa) with a small amount of [181]Hf (total Hf contant ca. 300 ppm) and charging it electrolytically with hydrogen. The hydrogen concentration was determined after the experiment by high-temperature vacuum extraction and was found to be 0.1 at. %. Figure 1 shows PAC spectra for [181]HfTa samples which were rapidly immersed from room temperature into liquid He. It is seen that the hydrogen-charged sample shows a pronounced modulation (disturbance) of the angular correlation which is absent in the hydrogen-free sample. This indicates that the disturbance in the upper spectrum is due to hydrogen trapped at [181]Hf. An annealing experiment showed that the disturbance disappeared irreversibly around 55 K indicating a break up of Hf-H. From the breakup temperature a binding energy of approximately 120 meV can be estimated. The HfTa system is similar to Ti in Nb (group-IV element in a group-V matrix) for which also a positive binding energy was found.[9]

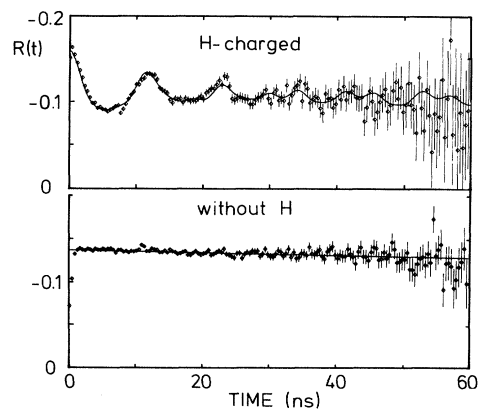If the sample was slowly cooled from room temperature to 4 K no disturbance was found. This can be ex-

FIG. 1. PAC spectra of [181]HfTa with and without hydrogen at $T_M = 4.2$ K. In both cases the sample was rapidly immersed from room temperature into liquid helium. The disturbance in the upper spectrum is attributed to hydrogen trapped at [181]Hf.

plained in the following way: At room temperature and low concentrations, hydrogen in Ta is in the α phase, i.e., statistically distributed. After immersion of the sample in liquid helium, the β-phase hydride tends to precipitate. However, on the way to the precipitates some of the hydrogen atoms are trapped at Hf. If the sample is slowly cooled the precipitations occur already at higher temperatures ($T > 55$ K) at which Hf cannot bind hydrogen, and no hydrogen is left in the α phase when finally the low temperature is reached. Thus rapid cooling is necessary to obtain trapping.

The disturbance in the upper spectrum of Fig. 1 is dominated by quadrupole interaction around $\nu_Q = 320$ MHz, $\eta = 0.8$ with a distribution of $\pm 10\%$. Here $\nu_Q = eQV_{zz}/h$ and $\eta = (V_{xx} - V_{yy})/V_{zz}$ was used. Q is the quadrupole moment of the nuclear state and V_{ii} are the components of the diagonalized electric field gradient. In addition a small fraction of probe atoms (ca. 10%) see a disturbance with $\nu_Q = 580$ MHz, $\eta = 0.23$. Both interactions are clearly different from $\nu_Q = 433$ MHz, $\eta = 0.45$ as obtained[8] for the β phase of Ta-H and therefore exclude a β-phase configuration. Calculations with the point-charge model and adjustment of the strength of the interaction to the known value for the β phase suggest that the interaction with the low η value could be identified with a single hydrogen atom whereas the other one should be due to two or more hydrogen atoms around the probe atom (tetrahedral sites were assumed). Concentration considerations limit the maximum number of trapped hydrogens to less than approximately three per Hf atom.

Figure 2 shows the fraction f of probe atoms which see a disturbance (sum of the two fractions). The decrease of f in Fig. 2 from the constant value f_0 at lower temperatures reflects directly the jump probabili-
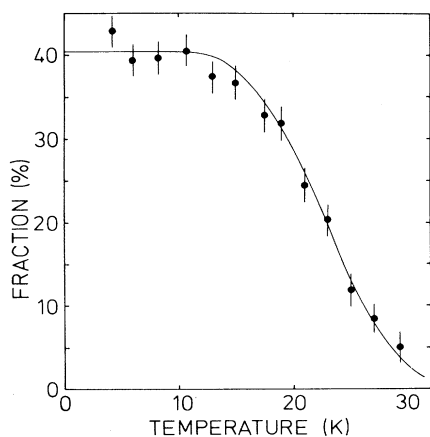
ty of hydrogen away from the probe atom. The characteristic time of the experiment is the nuclear lifetime of the isomeric state in Ta ($\tau_N = 25.7$ μs). The PAC experiment measures the probability that after this time hydrogen is still or again near the probe atom. The relative fraction of disturbed atoms f/f_0 (Fig. 2) is given by

$$f/f_0 = \tau_c/(\tau_c + \tau_N), \qquad (1)$$

where τ_c is the correlation time (an exponential decay of the correlation was assumed). τ_c is related to the diffusion parameters of hydrogen. If hydrogen starts at $t = 0$ from a nearest-neighbor tetrahedral site around the probe and if it diffuses over tetrahedral sites,[10] then with the additional assumption that the probability of return can be neglected one obtains

$$\tau_c = 4\bar{\tau} \text{ and } D = a_0^2/48\bar{\tau}, \qquad (2)$$

where $\bar{\tau}$ is the mean residence time, D the diffusion coefficient, and a_0 the lattice constant of Ta. The factor 4 accounts for the fact that only one out of four jumps leads away from the probe atom.

The data in Fig. 3 were deduced from the experimental quantities f/f_0 via Eqs. (1) and (2). The possibility that more than one hydrogen atom are around the probe atom and the probability of return of a hydrogen atom were neglected in this analysis. Both ef-

FIG. 2. Fraction of probe atoms which are disturbed by a hydrogen atom as function of temperature. The hydrogen concentration was 0.1 at.%.
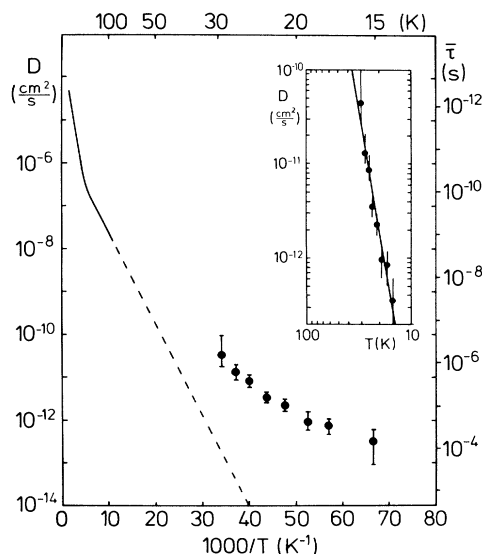

FIG. 3. Diffusion coefficient D of hydrogen in Ta in the α phase. Only statistical errors are shown. For systematic errors see text. The right-hand scale gives the mean residence time assuming that hydrogen jumps between neighboring tetrahedral interstitial sites. The solid line in the upper left corner represents the published diffusion data[1] and the dashed line an extrapolation of these data assuming an Arrhenius function. In the inset the present data are shown on a log-log scale. The solid line shows a T^7 law.

fects go in the same direction and cause the present analysis to underestimate the diffusion coefficient of hydrogen. Thus the present data represent lower limits for the diffusivity in the α phase.

The results for the diffusion coefficient D and the mean residence time $\bar{\tau}$ are shown in Fig. 3 as closed circles. In the upper left part of the figure, the published data[1] of the hydrogen diffusion in Ta are indicated as a strong solid line. These data show the famous break in the Arrhenius function which was interpreted as a change in the diffusion mechanism from a classical over barrier hopping at high temperatures to a tunneling process at lower temperatures. A similar change in the slope of the Arrhenius function was observed also in Nb.[1] The present data show a much faster diffusion of H in Ta than indicated by the extrapolation of the data of Ref. 1 with an Arrhenius function (Fig. 3). Thus either a much lower activation energy (20 meV instead of 42 meV) or a different law for the temperature dependence must be assumed.

The tunneling process can be described in the framework of the small-polaron hopping model[11-13] which predicts for T larger than the Debye temperature an Arrhenius behavior and for T much smaller than the Debye temperature a power law[11-13] with T^7, T^3, or T^1, depending on the details of the diffusion process. Therefore, an alternative representation of the data is given in the inset of Fig. 3 on a log-log plot. It can be seen that a T^7 dependence (solid line) is consistent with the data, but not a T^3 or T^1 dependence. However, it cannot be excluded that the present data lie in a transition region from an Arrhenius behavior to a power law with a small exponent. Thus the general concepts of the quantum mechanical diffusion process are confirmed by the present data but there remain open questions concerning the quantitative understanding.

The diffusion coefficients measured in the present experiment are several orders of magnitude larger than those given by Engelhard.[6] This indicates that the data in Ref. 6 are strongly influenced by impurities or inhomogeneities and that the observed recovery step at 42 K in Ref. 6 is due to the detrapping (e.g., from substitutional impurities) rather than to intrinsic diffusion.

In the present experiment for the first time the diffusion coefficients of hydrogen in Ta were measured at temperatures well below 100 K. This was possible by the application of a new method which uses the radioactive decay of ^{181}Hf to ^{181}Ta to trap hydrogen by an impurity and to release it after the nuclear conversion. It is planned to extend the experiments to low temperatures ($T < 1$ K) where delocalization effects (band propagation) may show up.[3,4] In addition, measurements with other hydrogen isotopes are in preparation. The experimental method can be applied to other systems for which appropriate PAC probes exist.

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