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Neutron-quasielastic-scattering study of hydrogen diffusion in a single crystal of tantalum*

J. M. Rowe

Institute for Materials Research, National Bureau of Standards, Washington, D.C. 20234† *and Solid State Science Division, Argonne National Laboratory, Argonne, Illinois 60439*

J. J. Rush

Institute for Materials Research, National Bureau of Standards, Washington, D.C. 20234

H. E. Flotow

Chemistry Division, Argonne National Laboratory, Argonne, Illinois 60439

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The diffusion of hydrogen in a single crystal of bcc tantalum ($TaH_{0.02}$) at 584 K has been investigated by neutron-quasielastic scattering at a variety of crystal orientations, and over a range of wave-vector transfer $|\vec{Q}|$, from 0.8 to 2.5 Å^{-1}. A detailed analysis of the observed quasielastic line shapes and widths shows that the results cannot be fitted by any simple jump-diffusion model involving instantaneous jumps between octahedral and tetrahedral interstitial sites. The quasielastic width curves (full width at half-maximum versus $\vec{Q}$) are much more isotropic than those predicted by any of the hydrogen-jump models, although the general shape of the widths at large Q is closer to that predicted by a tetrahedral-site model. These results are in distinct contrast to a recent neutron study of hydrogen diffusion in single-crystal (fcc) palladium, where the details of the quasielastic scattering were fitted well by a model assuming instantaneous jumps between octahedral sites. The $TaH_{0.02}$ quasielastic peaks suggest a diffusion "relaxation time" between 1 and 2 ps at 584 K. Analysis of the data also provides an average "mean-square hydrogen vibration amplitude" of 0.040 Å^2. The present single-crystal results are in reasonable agreement with the results of a previous neutron study of polycrystalline (α-phase) TaH_x. In addition, a value for the macroscopic diffusion constant at 584 K of 2.8×10^{-5} cm^2 s^{-1} is derived from the low-Q results, which is in excellent agreement with the value predicted from Gorsky-effect measurements.

I. INTRODUCTION

The diffusion of hydrogen in transition metals has been studied extensively, along with the effects of hydrogen on the structure and other properties of these metals.[1] Recently, it has been shown that neutron-quasielastic-scattering measurements can provide direct information on the diffusion of hydrogen atoms in metals, including the geometry and relaxation times of individual diffusive jumps or steps,[2] particularly for cases in which diffusion constants are $\gtrsim 10^{-5}$ cm^2 sec^{-1} (i.e., for relaxation or residence times $\tau \sim 10^{-10}-10^{-13}$ sec).

There has been a great deal of research by different techniques in the past few years on the diffusion of hydrogen in the group-VA refractory metals (V, Ta, Nb).[1,2] Very recent neutron studies[2] of powdered samples of VH_x[3] and TaH_x[4] and single crystals of $NbH_{0.07}$[2,5] in their α (bcc) phases have provided information on the residence times, concentration dependence, and activation energies for hydrogen diffusion. These studies also generally suggest the predominance of tetrahedral sites in the diffusion process, but in no case is there satisfactory agreement between the quasielastic-scattering results and the theoretical results calculated on the basis of a simple jump-diffusion model. The results for these bcc metals are in sharp contrast with the results of neutron studies on hydrogen in fcc palladium ($PdH_{0.03}$), in which a simple jump-diffusion model (for proton jumps between octahedral sites) provides a very good fit to the details of the quasielastic-scattering data.[6,7]

In the work reported here, we have extended our investigation of the tantalum-hydrogen system[4] to a detailed quasielastic-scattering study of the diffusion of a "defect" (2 at.%) concentration of hydrogen in a single crystal of tantalum. Such measurements on single crystals yield a much more comprehensive data set for comparison with theoretical models, since results are obtained as a function of the wave-vector transfer $\vec{Q}$. The observed spectra are not averaged over crystallite orientations, and thus most of the usual complications in the analysis of polycrystal data are avoided. In our fitting procedures and theoretical comparisons, we have carefully analyzed both the line shapes and widths of the measured quasielastic peaks.

II. EXPERIMENTAL

The sample used was a commercially obtained cylindrical single crystal of tantalum (10.0 cm long, 0.6 cm diam) of stated purity 99.996%, oriented so that a [110] crystallographic axis was along the cylinder axis. The specimen was contained in an aluminum holder which was mounted in an evacuated furnace. The sample and container could be rotated about the [$1\bar{1}0$] axis, allowing complete coverage of momentum transfer vectors of the form (ξ, ξ, η). The temperature was monitored by two iron-constantan thermocouples and was maintained during the entire experiment at 584 ± 5 K with a gradient of less than 0.7 K/cm over the length of the crystal. Blank runs were taken at seven crystal orientations before loading the sample with hydrogen. The crystal was then removed from the container, loaded with hydrogen, and replaced in the container in the same orientation (with respect to the container) as before.

In the loading procedure, hydrogen produced by thermal decomposition of UH_3 was allowed to diffuse into the tantalum crystal at 440–475 °C over a period of 14 h. The sample temperature was then lowered to room temperature over a 3-h period. It was determined from the initial and final volumes of hydrogen in the system that 121.4 cm^3 of H_2 reacted with the crystal (weight = 98.66 g), so that the H-to-Ta ratio was 0.0199 ± 0.0002.

The neutron spectra were measured on the thermal neutron time-of-flight spectrometer[8] at the CP-5 reactor at Argonne National Laboratory. The incident energy used was 5.0 meV with a resolution [full width at half-maximum (FWHM)] of 0.26 meV for elastic scattering as measured by the scattering from a vanadium cylinder of the same diameter as the sample. The data were obtained using a correlation chopper,[9] and after decorrelation were analyzed using the standard-data reduction programs described previously.[10] No corrections were made for multiple scattering, as this effect is small because of the large absorption and small scattering of the present sample. The data for different detectors and crystal orientations were normalized relative to each other, but no absolute normalization was attempted.

Data were collected at seven different orientations ψ of the single crystal with respect to the incident beam (ψ is defined as the angle between the [001] axis and the incident beam). The angles chosen were $\psi = 45°$, 30°, 15°, 0°, −15°, −30°, and −45°. For each orientation, spectra at fifteen angles of scattering between 30° and 108° were recorded simultaneously. With this choice of experimental parameters, the range of magnitude of the wave-vector transfer $|\vec{Q}|$ (for elastic scattering) covered was 0.8 to 2.5 Å^{-1}, while the direction of $\vec{Q}$ was reasonably well distributed over the 90° sector of reciprocal space containing the three crystal-symmetry axes for each value of $|\vec{Q}|$.

III. RESULTS AND DISCUSSION

Examples of the symmetrized scattering functions $\tilde{S}(Q, \omega)$ in the small energy transfer region are shown in Fig. 1. The value of Q ($|\vec{Q}|$) indicated for these examples is for purely elastic scattering ($\Delta E = 0$); no correction has been made for the variation of Q with energy transfer, which

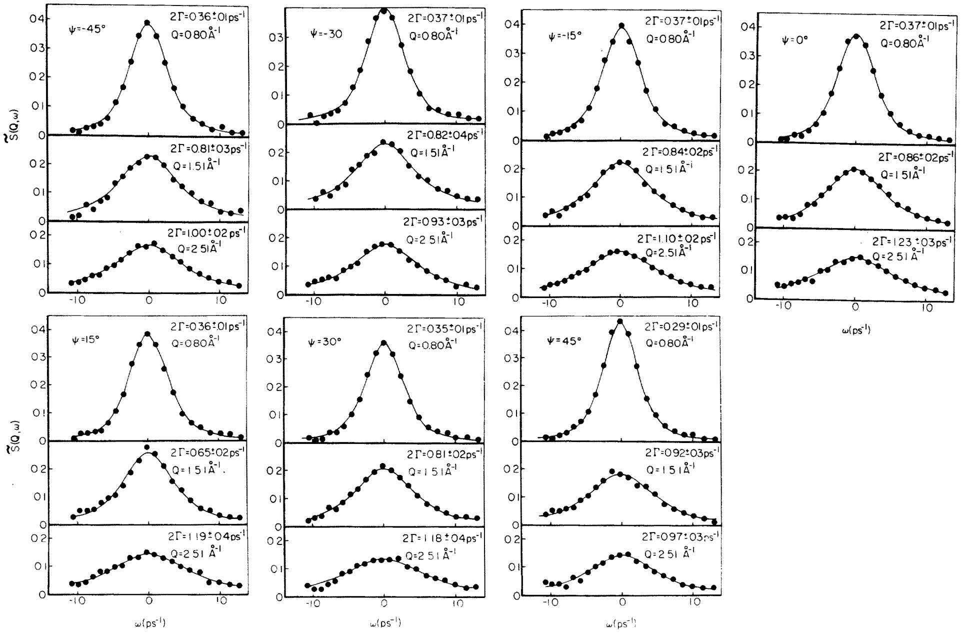

FIG. 1. Symmetrized scattering laws $\tilde{S}(\vec{Q}, \omega)$ vs ω for $TaH_{0.02}$ at 584 K for several values of momentum transfer ($\vec{Q}$) and crystal orientation ψ. Solid lines represent the resolution-broadened Lorentzians fitted as described in the text.

would be less than 5% for the range of energy transfers shown. We have also neglected the energy dependence of the absorption of the scattered beam, an effect of order 3% for the worst case. The solid curves shown represent the results of the fitting procedures described below.

As has been discussed in a number of papers,[2–7] the small energy transfer or quasielastic scattering can be written

$$\tilde{S}(\vec{Q},\omega)=\epsilon^{-\alpha Q^2}\, S_D(\vec{Q},\omega) \quad , \tag{1}$$

where α is the mean-square displacement of the hydrogen atom around its equilibrium interstitial site, and $S_D(\vec{Q},\omega)$ represents the shape of the quasielastic peak broadened by jump diffusion of hydrogen to alternative equilibrium sites. This expression is approximate and assumes that vibrations about the equilibrium sites are completely decoupled from jumps to new sites. If the further assumption is made that the jump itself is instantaneous, expressions for $S_D(\vec{Q},\omega)$ can be derived in which the average time τ between jumps and the site geometry are parameters. In this case, the dependence of the energy width of $S_D(\vec{Q},\omega)$ upon $\vec{Q}$ can lead to a direct determination of the site geometry in simple cases (e.g., for H in fcc Pd, where the hydrogens have been shown to jump between a Bravais lattice of octahedral sites[6,7]), and to the average rate of jumping, τ^{-1}. On the other hand, as discussed extensively in earlier work,[2–5,11] $S_D(\vec{Q},\omega)$ for hydrogen diffusing in a bcc metal should be comprised of a sum of Lorentzians with $\vec{Q}$-dependent widths and weighting factors depending on the type of occupied interstitial sites. The interpretation of the width curves then becomes much less straightforward. In this case, the observed variation of the width of $S_D(\vec{Q},\omega)$ depends in a complicated manner on the resolution used (the relevant parameter is $\Delta\omega_R\tau$, where $\Delta\omega_R$ is the resolution width).

In order to test the applicability of the two most probable simple jump models for hydrogen in Ta, i.e., jumps between octahedral or tetrahedral equilibrium sites, we chose first to fit the detailed shape of the measured quasielastic peaks directly to the predictions of these models with the residence time τ as a parameter, rather than to simply extract widths.[3–5]

The results of fitting both the octahedral and tetrahedral site models to the data for $\psi = -30°$ are shown in Fig. 2. These particular results are shown, since this is the angle for which the models work *best*. In the fitting procedure, the parameters varied were the residence times τ and a normalization constant for each angle of scattering. The values of τ found were 1.79 and 1.16 ps for the octahedral and tetrahedral models, respectively. These values are consistent with the τ of 1.6 ps derived from our previous polycrystal measurement (at 613 K) for $TaH_{0.15}$. From the figure, it can be seen that neither model works well at the large values of $|\vec{Q}|$ shown, where the models are most different. Moreover, the best values of τ found for different angles ψ were quite different. Extending the models to allow second-neighbor jumps or mixed-site occupancy[3] did not change this result. From these results, we conclude that no simple jump model based upon octahedral and/or tetrahedral sites can reproduce the data for $TaH_{0.02}$. This conclusion is supported by the analysis presented below.

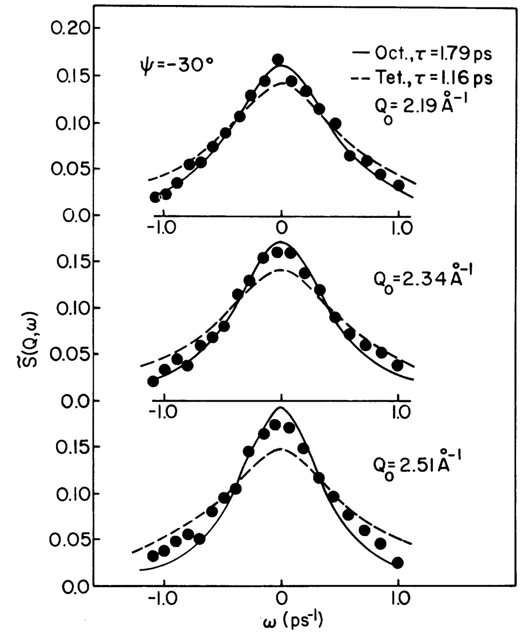

FIG. 2. Comparison of experimental scattering laws $\tilde{S}(\vec{Q},\omega)$ with line shapes predicted for the octahedral and tetrahedral jump models.

In an attempt to further elucidate the problem, we then proceeded to fit the data to a single resolution-broadened Lorentzian with the width of the Lorentzian as the fitting parameter. Surprisingly good fits were obtained, as can be seen from Fig. 1 where the solid lines represent the results of this fitting procedure. The particular examples of measured $S(\vec{Q},\omega)$'s shown are in no way unique; similarly good fits were obtained for *all* of the 105 independent quasielastic spectra. The failure of the octahedral and tetrahedral models to reproduce the data can be most readily understood by an examination of the FWHM of the Lorentzians obtained from these fits as a function of $\vec{Q}$.

The Lorentzian widths obtained at each crystal orientation ψ are shown as a function of $|\vec{Q}|$ in Fig. 3. Also shown in the figure are the values for the widths of $S_D(\vec{Q},\omega)$ predicted by the simple

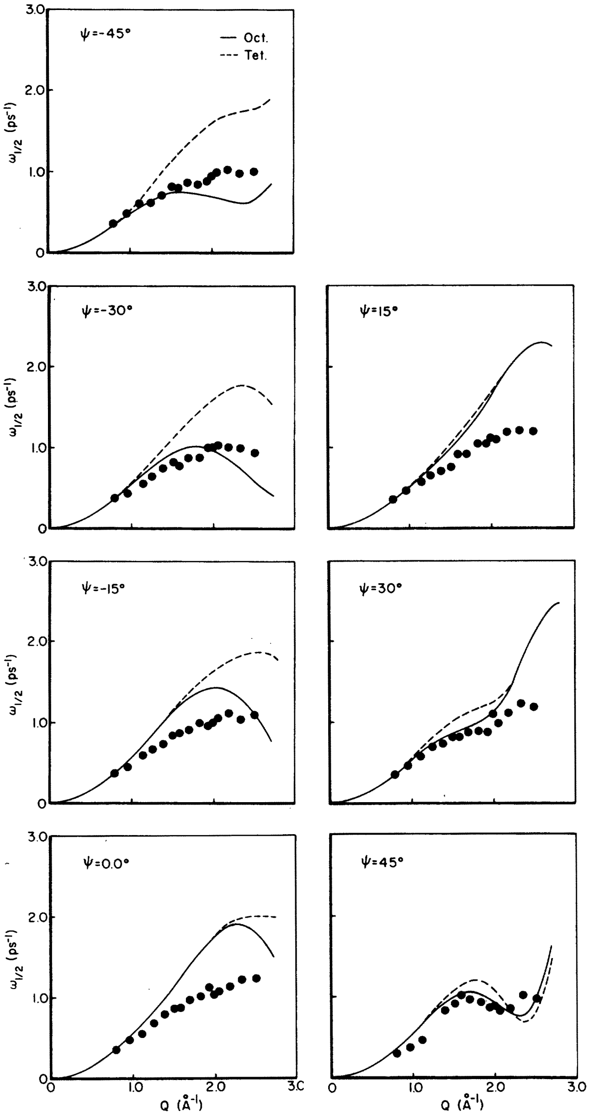

FIG. 3. Experimental full widths at half-maximum, $\omega_{1/2}$, vs $|\vec{Q}|$ measured for the various crystal orientations. Theoretical linewidths for the octahedral and tetrahedral models normalized as described in the text are also shown.

octahedral and tetrahedral jump models. The model widths were obtained by noting that for all models, the width at small $|\vec{Q}|$ becomes isotropic, so that $S_D(\vec{Q}, \omega)$ has the form of a single Lorentzian of width $2DQ^2$, where D is the macroscopic diffusion constant. Experimentally the measured width became independent of crystal orientation for $|\vec{Q}| = 0.80$ Å^{-1} (except for $\psi = 45°$), and the value of the average width obtained at this Q was used to choose the parameter τ for each model. The model predictions of $S_D(\vec{Q}, \omega)$ were then folded over the known resolution, and the width of a single Lorentzian giving the same over-all FWHM was chosen. Thus, the models and the data were treated in exactly the same way. We note here that this was exactly the method used to determine the τ's in our earlier work on fcc PdH$_{0.03}$,[6] where the resultant fit of octahedral-site model widths to measured widths was very good for all values of $\vec{Q}$. As can be seen from the figure, this is far from true in the present case. Both models show a $\vec{Q}$ dependence of the width which is quite different from that obtained experimentally, and the reasonable agreement between the octahedral model and the data for some values of ψ must therefore be considered fortuitous. From the figure, it can readily be seen that the data is much less anisotropic than the model predictions.

In order to emphasize this point, the results for two values of $|\vec{Q}|$ are shown in Fig. 4 as a function of the angle ϕ between $\vec{Q}$ and the [110] direction (note the distinction between ϕ and ψ). The values of ϕ for the [110], [111], and [001] directions are indicated on the figure. It should be noted that these are symmetry directions and that the widths must show local minima or maxima at these points, as is indicated by the models, which have cubic

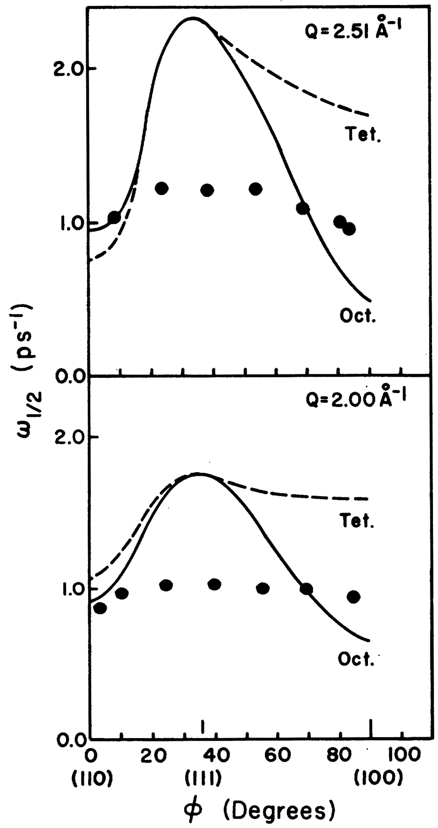

FIG. 4. Experimental linewidths vs ϕ (angle between $\vec{Q}$ and the [110] crystal direction) derived as described in the text. The predictions of the octahedral and tetrahedral jump models are shown for comparison.

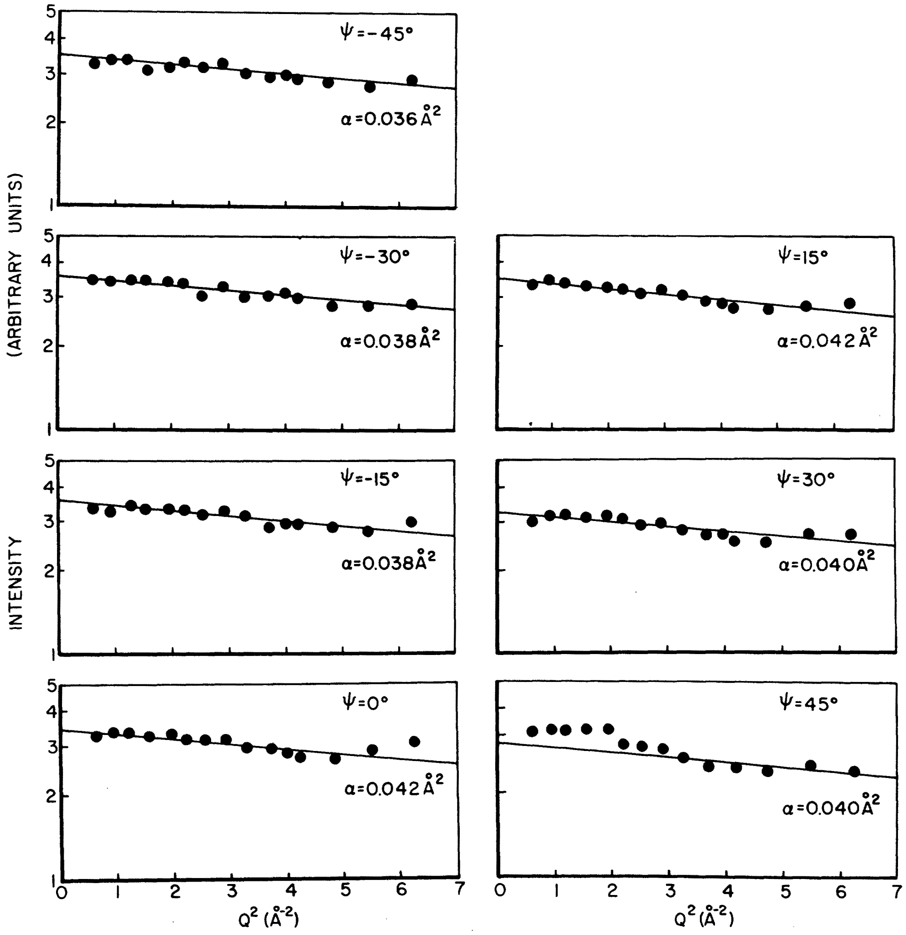

FIG. 5. Integrated quasielastic intensity plotted vs Q^2 for the various crystal orientations. Values of the derived parameter α are shown for each case.

symmetry.

The data points shown represent smoothed values taken from the results in Fig. 3 by drawing a smooth curve through the points in order to avoid large statistical fluctuations. Although the data points provide clear evidence of anisotropy and have the correct cubic symmetry, they show that the actual widths from the sample are much more isotropic than those predicted by the models. Further, this conclusion was not changed by extending our calculations to models which include mixed-site occupation or second-neighbor jumps.[3] It is also clear from this figure that the tetrahedral model is much less anisotropic than the octahedral model, and thus more consistent with the general shape of the width curves (Figs. 3 and 4). This observation, as well as the observed experimental widths, are in reasonable agreement with the results of our earlier quasielastic-scattering study of TaH_x polycrystals.[4] As in the single-crystal experiment, the tetrahedral model, when applied to the polycrystal results, provides a better fit to the width curves at large Q (although the octahedral model gave better agreement with the small Q results). It is interesting to note that the recent neutron study of hydrogen diffusion in a single crystal of bcc $\mathrm{NbH}_{0.07}$[5] showed significantly greater anisotropy in the measured quasielastic widths.

From the present data it is also possible to derive the value of α (Eq. 1). In Fig. 5, the total intensity of the observed quasielastic scattering is shown as a function of Q^2 for the seven values of ψ. Note that for $\psi = 45°$, the points do not follow the expected trend at $Q^2 < 2.0$ Å^{-2}. This observation may explain the inconsistency of the results shown in Fig. 3 for $\psi = 45°$ compared to results at the other crystal orientations. For this orientation the measured widths fall significantly below the model predictions below $Q = 1$, while the results at all other ψ's are in reasonable agreement. This is particularly obvious at $Q = 0.8$ Å^{-1}, where the measured width for $\psi = 45°$ is 15–20% below that for all other orientations (see Fig. 1). This suggests that there was extra elastic scattering at this orientation for the smallest Q's which did not subtract out with the blank. For this reason, the results for $\psi = 45°$ should be considered suspect, especially at small Q. As can be seen in Fig. 5, there is very little anisotropy in the derived α's. The mean value obtained is $\alpha = 0.040$ Å^2, in good agreement with the values derived from our polycrystal results for $TaH_{0.15}$, where $\alpha \sim 0.04$ Å^2 at $T = 613$ K. As discussed in the earlier paper,[4] this is close to the value predicted from the measured vibrational frequencies, in marked contrast to previous results for VH_x.[3]

As a final comparison, we have calculated the macroscopic diffusion constant D at 584 K from the derived Lorentzian width (0.36 ps^{-1} at the lowest Q measured (0.80 Å^{-1}) using the expression $2\Gamma = 2DQ^2$. The resulting "neutron" value is 2.8×10^{-5} cm^2 s^{-1}, which is in excellent agreement with the value of 2.7 ± 0.4 cm^2 s^{-1} calculated using the diffusion coefficients and activation energies derived from Gorsky-effect measurements on $TaH_{<0.04}$.[12]

IV. SUMMARY AND CONCLUSIONS

The diffusion of hydrogen in a single crystal of tantalum ($TaH_{0.02}$) has been studied by neutron-quasielastic-scattering measurements over a wide range of scattering angles and crystal orientations. A detailed analysis of the shapes and widths of the measured quasielastic peaks shows that the data cannot be fitted by any simple jump-diffusion model involving instantaneous jumps between octahedral and tetrahedral interstitial sites in the bcc metal lattice, even if second-neighbor jumps or mixed-site occupancy are assumed. This result is in sharp contrast to a recent neutron study of hydrogen diffusion in a single crystal of (fcc) palladium,[6] in which the quasielastic-scattering data were fitted well by a model assuming jump diffusion between near-neighbor octahedral sites. The most significant contrasts between the theoretical and experimental results for $TaH_{0.02}$ are: (i) The quasielastic width curves (versus $\vec{Q}$) are generally much more isotropic than that predicted by any of the hydrogen-jump models, and (ii) all of the measured quasielastic peaks are reproduced quite well by a fit assuming a *single* Lorentzian component, contrary to the multi-Lorentzian quasielastic peaks predicted by the jump models.

The experimental results for the $TaH_{0.02}$ crystal are consistent with our previous neutron study of polycrystalline TaH_x. As in the polycrystal results, the general shape of the widths (FWHM) versus Q at large Q for the single crystal are generally closer to that predicted by the tetrahedral model, while the octahedral model gives better agreement at small Q. The "best" τ values extracted from single-crystal line-shape fits for the tetrahedral and octahedral models (1.2 and 1.8 ps, respectively), are close to the value of 1.6 ps derived from the results for polycrystalline $TaH_{0.15}$ at 613 K. In addition, the average α ("mean-square vibration amplitude") value of 0.040 Å^2 derived from our single-crystal data is in good agreement with the polycrystal values. The single-crystal results, however, provide a much more rigorous test of the theoretical models (again illustrating the desirability of single-crystal measurements in detailed diffusion studies), and render even more uncertain the tentative conclusion[4] that tetrahedral sites are dominant in the diffusion of hydrogen in tantalum. Finally, the value for the diffusion constant, derived from the Lorentzian linewidths at the lowest Q measured (0.8 Å^{-1}) is in excellent agreement with macroscopic diffusion results.[12]

There is no obvious explanation for the line shapes and isotropic character of the quasielastic width curves observed in the present experiment. The results could be explained in part by assuming that the interstitial sites occupied by the hydrogen atoms are not well localized. Clearly more work, both theoretical and experimental, will be necessary in order to attain a detailed understanding of hydrogen diffusion in tantalum (and in other bcc metals). We will shortly extend our measurements on the $TaH_{0.02}$ single crystal to larger momentum transfers to provide a wider range of data for theoretical analysis. In addition, we will attempt to calculate theoretical scattering laws for comparison with the experimental data by molecular dynamics calculations under a variety of conditions.

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†Permanent address.

[1] For a survey of recent work on hydrogen in metals by a variety of techniques see, *Proceedings of the International Conference on Hydrogen in Metals, Julich, Germany, March,* 1972 (Kernforschungslange Julich GmBH, Julich, Germany, 1972), Vols. 1 and 2.

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