that the present results include the dominant contributions to the deformation potentials for those crystals in which the muffin-tin form for the potential is a good approximation to begin with.

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Neutron Quasielastic Scattering Study of Hydrogen Diffusion in a Single Crystal of Palladium*

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The diffusion of hydrogen in a single crystal of palladium ($PdH_{0.03}$) has been studied by quasielastic neutron scattering. The results provide the best evidence yet obtained for the applicability of a simple jump model of hydrogen diffusion in a metal and confirm the predominant occupation of octahedral sites in the Pd crystal, with a mean residence time at 623 K of 2.8 psec between jumps.

Recent neutron-scattering work on metal hydrides has demonstrated that quasielastic neutron-scattering measurements provide a unique opportunity to study the details of hydrogen diffusion on an atomic scale, including the geometry and relaxation times of individual diffusive jumps or steps. This is particularly true for hydrogen in transition metals in which the diffusion constants are $\lesssim 10^{-5}$ cm^2 sec^{-1} at several hundred degrees Celsius.

Until recently most of the quasielastic scattering measurements (e.g., on VH_x, NbH_x, and PdH_x) have been performed using powdered samples.[1,2] These experiments have provided considerable information on hydrogen diffusion, but since theoretical comparisons involve averaging over all crystalline orientations, it is difficult to establish rigorously the details of the diffusion process. The first quasielastic scattering measurement on hydrogen in a single crystal (in which the neutron momentum transfer $\vec{Q}$ can be well determined with respect to crystal direction) was reported quite recently[3] for 9% H in bcc niobium. Unfortunately the analysis of these results did not provide a firm conclusion on the details of the diffusion or the occupied sites. A

second experiment on 7% hydrogen in Nb,[4] with somewhat better incident-energy resolution, provided a reasonably good fit for $\vec{Q}$ along two symmetry directions ([110] and [111]) to a jump diffusion model with jumps between tetrahedral sites in the bcc lattice. However there are strong deviations from theory for $\vec{Q}$ in the [001] direction and, in addition, it was impossible to fit the quasielastic scattering widths versus crystal orientation at different values of $\vec{Q}$ with one jump relaxation time.

In this paper we present the first neutron quasielastic-scattering results on hydrogen in a single crystal of an fcc metal (3% H in palladium). The present results directly confirm earlier conclusions derived from measurements on powdered samples[5] that the hydrogen atoms in the Pd lattice occupy octahedral sites. More importantly, these results allow a detailed comparison with the predictions of a simple jump diffusion model[6] and show clearly that this model is a very good approximation to the behavior of hydrogen in palladium. This result is to be contrasted with that found earlier for the diffusion of hydrogen in bcc niobium.[3,4]

The single crystal of palldium used in these ex-

periments was 1.2 cm in diameter by 6 cm in length. The crystal was electrolytically loaded with hydrogen to a concentration of $PdH_{0.033}$ and sealed into an aluminum sample container. The ends of this sample container were fitted with heaters and thermocouples for temperature control. The sample was run at 623 ± 5 K.

The specimen was aligned to within 1° of arc on a conventional neutron diffractometer by measuring the (200) and (220) Bragg reflections, from which it was ascertained that the mosaic spread of the crystal with hydrogen added was less than $\frac{1}{4}$°. The major axis of the crystal coincided with a [001] crystallographic axis to within 2°. After alignment, the crystal was mounted on a turnta-

ble at the thermal-neutron time-of-flight apparatus at the CP-5 reactor of the Argonne National Laboratory. This turntable allowed rotation about the [001] axis of the crystal, and data were taken for four orientations about the axis—ψ = 0.0°, 22.5°, 45.0°, and 60.0°, where $\psi = 0$ corresponds to the incident beam entering the crystal along a [100] axis.

The incident energy used was 4.96 meV with an overall energy resolution of 0.25 meV (full width at half-maximum) as measured at the detector using an incoherent-elastic-scattering sample of the same geometry. Data were collected at fifteen angles of scattering (φ) simultaneously, over a range $14.4° < \varphi < 114.6°$, which corresponds
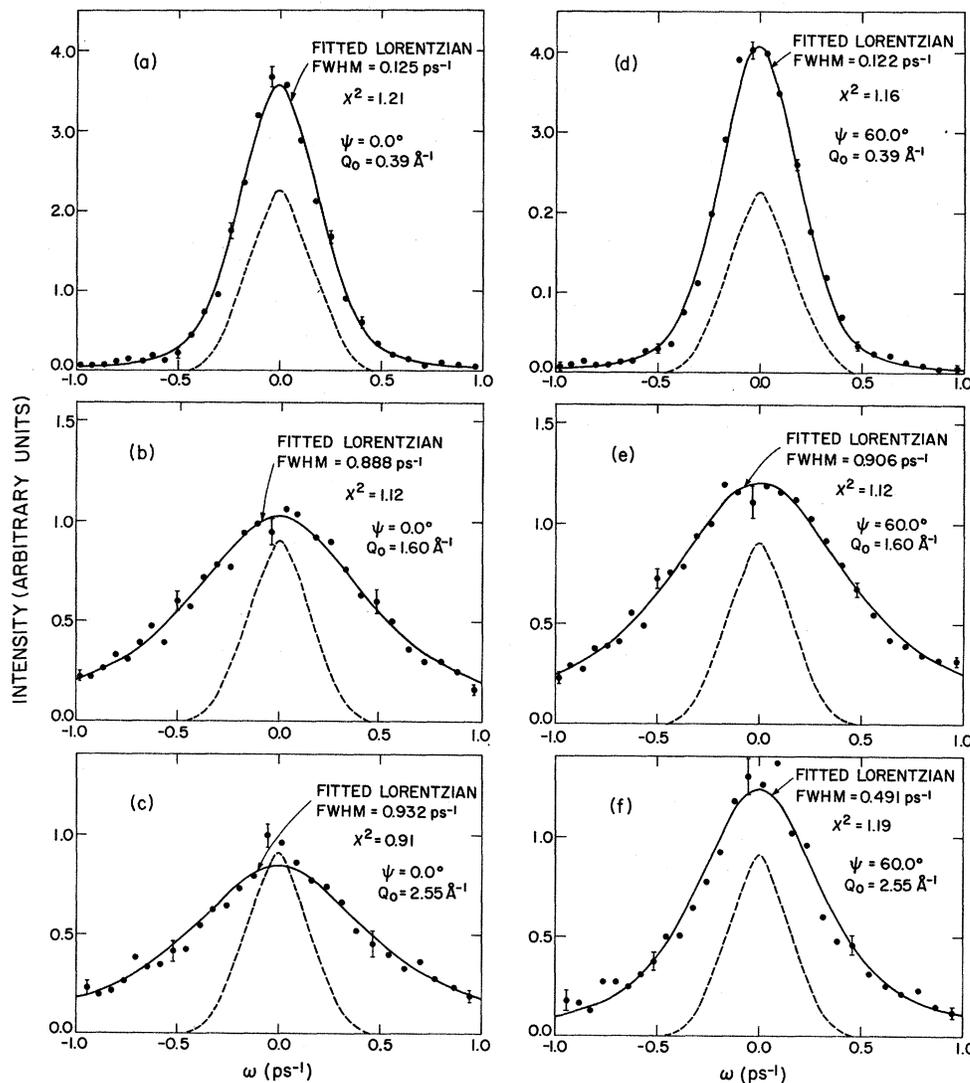
FIG. 1. Selected examples of the data obtained for two crystal orientations, along with the results of the fitting procedure described in the text. The dashed line represents the measured instrumental resolution function.

to wave-vector transfers Q of 0.39 Å^{-1} < Q < 2.60 Å^{-1}. The highest angle results were discarded because of contamination from a (111) Bragg reflection in the Al sample container.

The data collected at the four ψ values were corrected for sample-container and palladium scattering by subtracting the results from a similar Pd crystal run in the same sample holder at the same temperature. This correction was small, but not negligible. The data were then converted from time-of-flight spectra to an energy-transfer scale, and corrected for detailed balance. The inelastic one-phonon incoherent scattering from the hydrogen was subtracted by noting that the one-phonon cross section is constant in energy transfer for small values of energy transfer $\hbar\omega$ at constant wave-vector transfer Q. Thus, a constant value determined from the asymptotic behavior of the quasielastic scattering was subtracted at each angle.

Samples of the corrected data are shown in Fig. 1. The smooth lines on this figure represent the results of fitting a single Lorentzian broadened by the resolution function of the instrument (which is shown by the dashed lines in the figure). The widths of the Lorentzians which gave the best fit are shown on the figure, as are the values of χ^2 found from the fit, where χ^2 is the normalized sum of the squares of the deviations from the fitted curve divided by the variance of the experimental points. The values of χ^2 shown are typical of all the results obtained —the maximum value found for any curve was 1.54, which represents a good fit. The region of data to be fitted was determined by setting the criteria that the value of Q change by less than 5%, and that the scattered energy be close enough to the incident energy to allow us to neglect energy-dependent absorption effects. The compromise selected was to use -1.0 psec^{-1} < ω < 1.0 psec^{-1} (ω = energy transfer$/\hbar$). As can be seen from the figure, the broadened Lorentzians give a good representation of the data in every case.

Using the "best fit" Lorentzian width for each measurement, the data were interpolated in reciprocal space and the widths at half-maximum ($\Delta\omega_{1/2}$) along the symmetry directions [100] and [110] were obtained. The results of this interpolation are shown in Figs. 2(a) and 2(b), along with the predictions of the Chudley-Elliott theory[6]
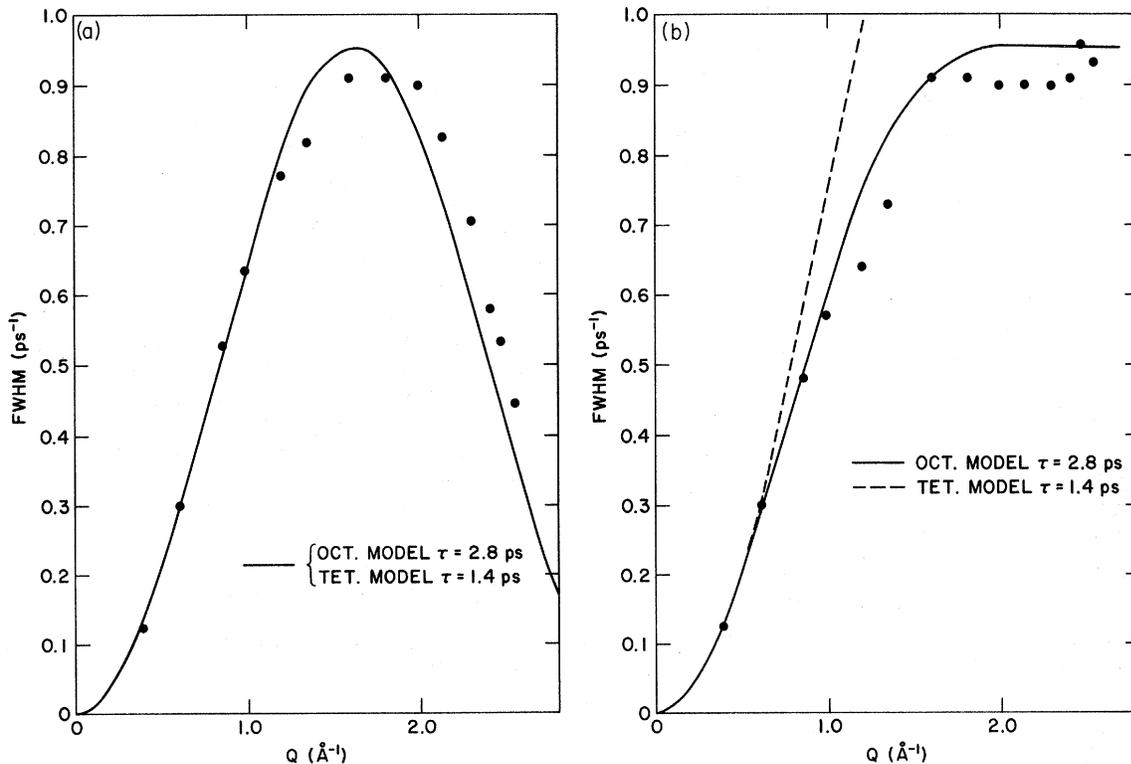
FIG. 2. (a) Full widths at half-maximum for $\vec{Q}$ along the [100] axis obtained by interpolating the widths determined by fitting. The predictions of a simple jump model for the two possible interstitial sites are shown as solid curves. (b) Same as in (a) for $\vec{Q}$ along the [110] axis.

for both octahedral and tetrahedral sites. This theory describes the diffusive process in terms of instantaneous jumps from any site to one of its nearest-neighbor sites with a probability per unit time $1/\tau$. When applied to a crystal for which the interstitial sites form a Bravais lattice (as in Pd), this theory predicts a cross section with a Lorentzian line shape. In this model, interactions between hydrogen atoms are neglected, and a complete decoupling of vibrational and diffusional motions is assumed. The values of the mean residence time between jumps, τ, were chosen to give good agreement at small momentum transfer. This criterion was chosen since the quasielastic widths are isotropic at small Q, and the results of the four independent measurements for $Q = 0.39$ Å^{-1} were in excellent agreement ($\Delta\omega_{1/2} = 0.125$, 0.127, 0.125, and 0.122 psec^{-1}). As can be seen from the figure, the theory assuming octahedral-site occupation with $\tau = 2.8$ psec is in good agreement with the data. Also, the fit of this model to the data for each of the four crystal orientations (with no interpolation) is at least as good as that shown in Fig. 2. The tetrahedral-site model is clearly ruled out.

The present data do not give very reliable information on the Debye-Waller factor $e^{-\rho Q^2}$ because of the high absorption cross section and the somewhat irregular crystal shape. However, the results do indicate that ρ is anisotropic with $\rho = 0.05$ Å^2 for the [110] direction and $\rho = 0.09$ Å^2 for the [100] direction. The accuracy of these values is not better than 20%, but the anisotropy is well established.

The present results are in reasonable agreement with the earlier work of Sköld and Nelin on polycrystalline samples. At 630 K, these authors found $\tau = 2.3$ psec, but gave no estimate for ρ except at 704 K ($\rho = 0.13$ Å^2). Extrapolating this value to 623 K gives $\rho \approx 0.12$ Å^2 which is significantly larger than the present estimates. The conclusions of Sköld and Nelin about octahedral-site occupation are fully confirmed by the present results. More importantly, the good agreement between all our results and the simple jump diffusion theory[6] shows that the migration of individual hydrogens in the fcc Pd lattice can be well described as instantaneous jumps between adjacent octahedral sites. This result suggests that interstitial hydrogen in other fcc metals would also diffuse in the same way. The slight deviation of our experimental widths at higher Q (Fig. 2) from the theoretical curves could be explained by one or more of a number of effects. These include the possibility of occasional second-neighbor jumps, the interaction of neighboring interstitial hydrogens, and the effect of finite jump times between sites (~0.1 psec for a free hydrogen atom compared to our τ of 2.8 psec). It should be noted that the low (3%) hydrogen concentration, better than factor of 2 lower than that used in previous single-crystal experiments,[3,4] should minimize the second of these effects.

Certainly the existence of deviations from theory offers an opportunity to learn more about the details of the hydrogen diffusion process in metals by a careful control of experimental conditions (metal structure, hydrogen concentration, temperature, etc.) and by an expansion of the theory to include these effects.

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[1]For a broad review of the recent work on the properties of metal hydrogen systems see the *Proceedings of the International Conference on Hydrogen in Metals, Jül-Conf.—6, Jülich, Germany, 20–24 March 1972* (Kernforschungsanlange Jülich GmbH, Jülich, Germany, 1972), Vols. 1 and 2. This conference proceeding also contains considerable information on previous neutron scattering measurements on metal hydrides.

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