MASTER

HYDROGEN DIFFUSION AND TRAPPING IN BCC AND FCC METALS

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INTRODUCTION

The behavior of hydrogen in metals is a subject of intense current interest (1,2,3) both for scientific as well as technological reasons. Recently, a number of practical applications like hydrogen storage in the form of metal hydrides or hydrogen as a working fluid in refrigeration devices have been considered. In particular, the properties of tritium in the construction materials as well as in the lithium blanket of future fusion reactors are investigated currently. This lecture restricts itself to the fundamental aspects of the metal-hydrogen systems. Here the large number of anomalous properties are the reason for continuous scientific effort. For instance, the time scale of hydrogen motion is extremely short. The characteristic frequencies of the localized modes of hydrogen in Ta, Nb, or V are in the order of 10^{-14} sec (energies between 0.1...0.2 eV); the jump frequencies for H-diffusion at elevated temperatures in those systems are between 10^{+12} to 10^{+13} sec $^{-1}$. They are comparable with the correlation times for diffusion in liquids and more than ten orders of magnitude larger than e.g. the jump times for nitrogen in Nb. Out of the large number of experimental data this paper will survey only some recent results on representative fcc and bcc metals for dilute H solutions. The first part of this lecture deals with the nature of the elementary step in H-diffusion. Here the temperature and isotope dependence of the H-diffusion coefficient gives hints to the mechanism involved. The experimental results are discussed in terms of semiclassical and quantum mechanical diffusion theories.

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Quasielastic neutron scattering reveals microscopic details of both the time and space development of the diffusive process on an atomic scale. After outlining the method on the example PdH_x in the second part of this lecture, new results on the jump geometry in bcc metals with special emphasis on the anomalous behavior at higher temperatures, where correlated jump processes are important, are presented. An examination of the Debye-Waller-factor shows a point-like localized proton at all temperatures. In part 3 we deal with the problem of H-vibrations in bcc metals and their possible conjunction to the fast diffusion mechanism. In particular, the dispersive step in the TA acoustic branch in $\text{NbH}_{0.15}$ (4) and the recently discovered energetically low flat phonon modes in $\text{NbD}_{0.85}$ (5) will be discussed (6).

The influence of substitutional and interstitial impurities on the hydrogen diffusion properties is treated in part 4 of this lecture. The trapping capability of point defects has been concluded firstly from increasing H-solubility with increasing amounts of impurities. Resistivity, internal friction and Gorsky-effect experiments reveal further evidence for the trapping process. Again, quasielastic neutron scattering gives insight into the microscopic details of the diffusion process in the presence of trapping impurities. Results on NbH_x doped with nitrogen impurities are interpreted in terms of a two-state model which includes multiple trapping and detrapping processes (7). In a second step the data are compared with numerical calculations using a realistic potential. The effect of substitutional impurities is demonstrated in the example of vanadium impurities in Nb. NMR and preliminary neutron results are presented.

Finally, the dynamical behavior of the hydrogen in the trapped state is surveyed. Internal friction experiments on H trapped on O-impurities at low temperatures seem to be in accordance with predictions of the tunneling hopping theory (8). Specific heat experiments on NbN_xH_y -systems show a Schottky-type anomaly at about 1 K with a strong isotope effect (9). These results are explained in terms of tunneling states of the proton in the neighborhood of the impurity.

TEMPERATURE AND ISOTOPE DEPENDENCE OF THE H-DIFFUSION COEFFICIENT IN BCC V, Nb, AND Ta AND FCC Pd, Cu, AND Ni

The experimental methods to obtain the hydrogen diffusion coefficient can be divided into two groups according as it is measured by studying the relaxation of a nonequilibrium distribution to equilibrium or it is investigated under equilibrium conditions. The first group contains the commonly used macroscopic

methods like Gorsky-effect, permeation-, resistivity relaxation-, heat of transport-, outgassing experiments, etc. These methods have been reviewed elsewhere (3,10) and will not be described here. The second group comprises microscopic experiments like nuclear magnetic resonance, Mössbauer effect and quasielastic neutron scattering (QNS). The large number of experimental results obtained by the various methods have been compiled recently and are presented in Table 1 for our examples. In all cases, the data are represented in the form of an Arrhenius relation. $D = D_0 \exp -E_a/kT$ where E_a is the activation energy for the diffusive process. In the case of Pd and Ni, the various methods reveal remarkably consistent values for the diffusion constant. This can be attributed to the relatively well-defined surface conditions which lead to reliable results also for the different permeation techniques. In the case of the other materials, a good consistency of the data only exists if the results of surface independent methods are compared. For the case of H in Nb, Fig. 1 presents selected data obtained by the different methods (12-17). Some recent permeation results on Pd-plated Nb samples are included (18). Fig. 1 shows clearly the anomalous temperature dependence of the hydrogen diffusion constant in Nb which exhibits two different activation energies in the considered temperature region. An even more pronounced break in the temperature dependence of the diffusion coefficient has been reported recently for H in Ta (19). Whereas in Nb for deuterium no change of slope has been observed so far, there are experimental indications for this effect also for deuterium in Ta.

In vanadium, however, where the activation energy for diffusion has the lowest value of all three bcc-metals, no change of slope has been observed so far. Concerning the isotope dependence of diffusion coefficient which primarily gives hints to the nature of the diffusion mechanism we have the following situation for the 3 bcc-metals: H diffuses always faster than D and T in the whole temperature range investigated so far. The preexponential factors in the high temperature range are nearly independent of the isotope and if one corrects for the lattice constant a the preexponential $1/\tau_0 = D_0 a^2/48$ is also independent of the material. For the activation energies $E_H < E_D < E_T$ holds. The ratio of the diffusion coefficients of hydrogen and deuterium are in general far away from the classical prediction of the Vineyard theory (20): $D_H/D_D = \sqrt{m_D/m_H}$.

As an example for the temperature and isotope dependence of the diffusion coefficient in an fcc metal Fig. 2 presents the results for Pd. In contrast to the behavior in the bcc metals, where the jump rates increase with decreasing mass of the isotope (22), here D diffuses faster than H whereas the values

Table 1. Activation energies E and preexponential factors D_0 of the Arrhenius relation for the diffusion coefficient in the various metals.

System	E_a (meV)	$D_0 \times 10^4$ (cm^2/sec)	System	E_a (meV)	$D_0 \times 10^3$ (cm^2/sec)
Nb-H					
T>270K(11)	106	5.0	Pd-H(11)	230	2.9
T<250K	68	0.9	Pd-D(22)	206	1.7
Nb-D (11)	127	5.2	Pd-T(23)	276	11
Nb-T(11)	135	4.5	Cu-H(21)	403	11.3
Ta-H			Cu-D(21)	382	7.3
T>270K(11)	140	4.4	Cu-T(21)	378	6.1
T<200K(11)	40	0.02	Ni-H(21)	409	7.0
Ta-D(11)	160	4.6	Ni-D(21)	401	5.3
V-H(11)	45	3.1	Ni-T(21)	395	4.3

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Fig. 1. Diffusion coefficient for H, D, T in Nb. Heat of transport (14), Neutrons (16,17), resistivity (15), Gorsky effect (12,13) permeation (18).

Fig. 2. Diffusion coefficient of H-isotopes in Pd, H and D (22), T (23).

for T are below those of H (23). An extrapolation of the high temperature data of Katz et al. (21) on Ni and Cu would result in a similar reversed isotope effect for the diffusion coefficients at lower temperatures yielding $D_H < D_D < D_T$. For all three, fcc metals the preexponentials D_0 for H and D behave close to $\sqrt{m_D/m_H}$. This holds also for T in the case of Ni and Cu; i.e. $D_{0H}:D_{0D}:D_{0T} = 1:1/\sqrt{2}:1/\sqrt{3}$. Contrary to the bcc metals the activation energies decrease in going from H to T causing the reversed isotope effect at lower temperatures. In order to obtain evidence whether the hydrogen diffusion is described more likely by a classical over-barrier jump process (20) or by a quantum mechanically tunneling hopping process (24, 25) which are both reasonable for the investigated temperature and concentration region we shall compare the experimental results with predictions of both theories. The classical rate theory modified with respect to the discreteness of the hydrogen

excitations $\hbar\omega$ leads to the following results (21): (i) for $kT \ll \hbar\omega$ which is relevant for the bcc metals it predicts a universal prefactor independent of the isotope and with respect to the jump frequency also independent of the material. The activation energy is predicted to depend on the isotope. In its simplest form the isotope effect is only related to the different oscillation energies of the isotopes and is given by $E_D - E_H = 1/2 (\hbar\omega_D - \hbar\omega_H) = 1/2 \hbar\omega (1 - 1/\sqrt{2})$; (ii) for $kT \gg \hbar\omega$ the theory becomes identical with the classical Vineyard theory. (iii) For the intermediate region $2kT \sim \hbar\omega$ which applies to the fcc metals we refer to the full formula in Ref. (21). Concerning the bcc metals, the prediction of an isotope and material independent preexponential is fulfilled quite well by the experimental data (see Table I), if we do not consider the anomalous low temperature behavior of H in Nb and Ta. For the activation energies, we get e.g. for Nb $E_D - E_H = 1/2 \hbar\omega (1 - 1/\sqrt{2}) = 23$ meV (using the average value of $\hbar\omega = 155$ meV) which is very close to the experimental finding. For the change of the activation energy for H in Nb and Ta this theory has no explanation. For the fcc metals, the theory predicts roughly a $m^{-1/2}$ isotope effect in the prefactor in the temperature region under investigation which is again in agreement with the experimental results. To explain the reversed isotope effect of the activation energies, it was suggested (21) to assume higher frequencies of the localized modes in the saddle point configuration than in the minimum position. An analysis of the diffusion data of H, D, and T in Cu and Ni in terms of this concept revealed, however, unrealistic high-frequency values for the localized mode vibrations of the H atom. (Ni: $\hbar\omega = 330$ meV in the minimum and $\hbar\omega = 470$ meV in the saddlepoint configuration).

The tunneling hopping theory in its simplest form (24) predicts the following behavior: (i) For $T \ll \theta_D$ (θ_D : Debye temperature) the diffusion coefficient should be proportional to $J^2 T^7$, where J is the tunneling matrix element between adjacent sites and T is the temperature. For $T \approx \theta_D$ the theory predicts an Arrhenius behavior similar to the classical theory. The parameters, however, have another meaning. The prefactor is governed again by the tunneling matrix element J whereas the activation energy E_a is given by the energy necessary to distort the lattice in such a way that the diffusing particle has the same energy in the initial and final position. Again, we have to examine the experimental data with respect to predictions of the theory. First, we can state that for long-range diffusion of H and its isotopes a T^7 behavior has never been observed which is not very surprising concerning the investigated temperature region. The absence of an isotope effect in the prefactor found for the bcc metals above 250 K, however, is in contrast to the predictions of the theory, where the prefactor is dominated

by a strongly isotope dependent tunneling matrix element. The observed isotope effect in the activation energy $E_H < E_D$ again is in conflict with theory. For H and D in Nb the double-force tensors are equal (26) and no isotope effect should be expected. With respect to the double force tensors of H and D in Ta, a reversed isotope effect should have been observed (26). Thus, the tunneling hopping theory at least in its simplest form does not describe the experimental results for Nb and Ta above 250 K. An extension of the theory (25) using the concept of extended H wave functions in order to account for the outlined discrepancies is in disagreement with proton form factor measurements by neutron scattering (27). However, a recent reexamination of the small polaron tunneling hopping theory by Emin et al. (28) casts new light on the situation. This approach avoids previously made simplifications like a perturbation treatment of J, termed nonadiabatic regime, the so-called "Condon-approximation" which neglects the influence of the actual position of the host atoms on J, and finally, it includes excited states of the diffusing particle. Explicit calculations for the diffusion of the H isotopes including the positive muon in Nb revealed results as shown in Fig. 3. The following features should be noted: (i) the high-temperature activation energy of diffusion increases with increasing mass of the diffusing species; (ii) the adiabatic character of the high-temperature diffusion behavior manifests itself in the isotope independent prefactor; (iii) at lower temperatures, the contribution of nonadiabatic transfers which require a lower activation energy increases. This results in a change of slope in the Arrhenius plot of the H diffusion constant. Thus, the results are in very good agreement with the experimental finding and are the only theoretical calculations which can account for the change of slope observed for the H-diffusion constant.

Employing tunneling hopping theory beyond the Condon approximation and using pseudopotential results to describe the potential for H in Cu, very recently Teichler (29) could reproduce the experimental results for H-diffusion in this fcc-metal theoretically. For the more complicated transition metals Ni and Pd no theoretical calculations are available so far.

QUASIELASTIC NEUTRON SCATTERING STUDIES OF HYDROGEN DIFFUSION IN Pd, Nb, Ta, AND V

For the study of the diffusion of H in metals QNS is a unique tool (30) which allows the simultaneous investigation of the time and space development of the diffusive process on a microscopic scale. In the case of hydrogen which scatters predominantly incoherent such an experiment reveals information on the behavior of single protons in space and time. Following the

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Fig. 3. Calculated diffusion coefficients for the H isotopes in Nb (28).

concept of van Hove (31) the observed double differential cross section $\partial^2\sigma/\partial\omega\partial\Omega$ is proportional to the Fourier transform of the self-correlation function $G_s(\underline{r},t)$ of the proton

$$\frac{\partial^2\sigma}{\partial\omega\partial\Omega} \sim S_{\text{inc}}(Q,\omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} dt \int_{-\infty}^{+\infty} d^3r e^{i(Q\underline{r}-\omega t)} G_s(\underline{r},t) \quad (1)$$

where $S_{\text{inc}}(Q,\omega)$ is the so-called incoherent scattering law, $Q = \hbar K_f - \hbar K_i$ is the momentum transfer and $\hbar\omega = E_f - E_i$ is the energy transfer at the sample. In the classical limit $G_s(\underline{r},t)$ can be interpreted as the conditional probability to find a proton at a time t at a site $\underline{r}$ if it has been at $\underline{r} = 0$ for $t=0$. The results of QNS experiments on H-diffusion are commonly

interpreted in terms of the Chudley-Elliott model (CE) (32) which introduces the following assumptions:

(i) the jump time from site to site is small compared to the mean rest time of hydrogen on its interstitial site.

(ii) there is no correlation between vibration and jump processes.

Under these circumstances the self-correlation function can be obtained by solving a master equation:

$$\frac{\partial}{\partial t} G_s(\underline{r}, t) = \frac{1}{z\tau} \sum_{i=1}^z (G_s(\underline{r} + \underline{S}_i, t) - G_s(\underline{r}, t)) \quad (2)$$

where $\underline{S}_i$ are the jump vectors to the accessible neighboring sites, z is the number of these sites and τ the mean rest time at a certain site. Eq. (2) can be integrated by a Fourier transformation yielding in the case of Bravais lattices:

$$\frac{\partial}{\partial t} G_s(Q, t) = - \frac{1}{z\tau} \sum_{i=1}^z (1 - e^{iQ \cdot \underline{S}_i}) G_s(Q, t) \quad (3)$$

$$= \frac{1}{\tau} f(Q) G_s(Q, t)$$

$$G_s(Q, t) = e^{-\frac{t}{\tau} f(Q)} \quad (4)$$

$G_s(Q, t)$ fulfills already the appropriate initial condition. Finally, Fourier transformation with respect to the time yields

$$\text{Sinc}(Q, \omega) = \frac{1}{\pi} \frac{f(Q)/\tau}{\left(\frac{f(Q)}{\tau}\right)^2 + \omega^2} \quad (5)$$

The intensity of the quasielastic line can be described by a the Debye-Waller - or form factor $\exp - 1/3Q^2 \langle u^2 \rangle$, where $\langle u^2 \rangle$ is the mean-square displacement of the proton at its site. Using the diffusion of H in Pd as an example we outline briefly what kind of information can be obtained from an investigation

of the $\underline{Q}$ and ω -dependence of the quasielastic scattering law. Fig. 4 shows the two possible interstitial sites for hydrogen in fcc Pd together with the jump vectors to nearest-neighbor sites.

Table II summarizes some characteristics for the two possible jump mechanisms.

For equal diffusion coefficients we have $\tau_0 = 2\tau_t$. For both models the functions $f(\underline{Q})$ can be easily calculated yielding:

$$f_o(\underline{Q}) = \frac{1}{6} \left\{ 6 - \cos \frac{a}{2}(\underline{Q}_x + \underline{Q}_y) - \cos \frac{a}{2}(\underline{Q}_x - \underline{Q}_y) \right. \\ \left. - \cos \frac{a}{2}(\underline{Q}_x + \underline{Q}_z) - \cos \frac{a}{2}(\underline{Q}_x - \underline{Q}_z) \right. \\ \left. - \cos \frac{a}{2}(\underline{Q}_y + \underline{Q}_z) - \cos \frac{a}{2}(\underline{Q}_y - \underline{Q}_z) \right\} \quad (6)$$

$$f_t(\underline{Q}) = \frac{1}{3} \{ 3 - \cos \frac{a}{2} \underline{Q}_x - \cos \frac{a}{2} \underline{Q}_y - \cos \frac{a}{2} \underline{Q}_z \} \quad (7)$$

For small momentum transfers $\ll Q$ the width $\Gamma(\underline{Q}) = \tau^{-1} f(\underline{Q})$ of the Lorentzian is independent of the jump model $\bar{\Gamma}(\underline{Q}) = \hbar D Q^2$. It reveals the macroscopic diffusion coefficient measured over microscopic distances. The $\underline{Q}$ dependence of line width at large $\underline{Q}$'s is determined by the geometrical details of the jump mechanism. For fcc-Pd Fig. 5 shows the theoretical $\underline{Q}$ dependence of line width for the models in question. The experimental points (33) are clearly in favor for H jumps between nearest-neighbor octahedral sites. With respect to the high barrier and the large spacing between the interstitial sites this result is quite reasonable.

For the bcc metals with their complicated hydrogen sublattice (6 sites per unit cell)(Fig. 6), the situation is much more complicated. Besides the complication due to the non-Bravais-H-sublattice, there is experimental evidence that the diffusion process itself is not as simple as for the fcc metals. Already earlier results on V (34) Ta (35) and Nb (36) showed systematic deviations from the predictions of a simple nearest-neighbor jump model. Also, anomalies in the intensity of the quasielastic line have been reported (34,37). These anomalies have been attributed to the occurrence of further neighbor jumps and/or to jumps between different types of institial sites

Table II. Characteristics of tetrahedral and octahedral jump mechanism in fcc metals

	Octahedral model	tetrahedral model
Number of nearest neighbors	12	6
Jump direction	(110)	(100)
Jump length	$a/2\sqrt{2}$	$a/2$
Diffusion coefficient	$a^2/12\tau_o$	$a^2/24\tau_t$
$D = l^2/6\tau$

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Fig. 4. Possible H-interstitial sites in fcc-Pd, $\circ$ Pd atoms, $\times$ octahedral sites, $\circ$ tetrahedral sites, S_i H jump vectors.

(34,35) and to the influence of a finite time of flight (38) but no conclusive picture has been reached.

Very recently, Lottner et al. (27,39) have reexamined the problem for Ta, Nb, and V. Quasielastic neutron scattering experiments were performed at $NbH_{0.02}$, $TaH_{0.13}$ and $VH_{0.07}$ single crystals at temperatures between 290 and 760 K for Q values between 0.3 and $2.5 \text{ \AA}^{-1}$. The data were analyzed in terms of 4 different models always assuming that H jumps occur between tetrahedral sites.

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Fig. 5. Experimental results for the quasielastic line width in PdH_x for a (100) (left) and a (110) direction; solid line octahedral jump model, dashed line tetrahedral jump model (33).

Model (1): Hydrogen jumps occur only between nearest neighbor sites with jump vectors in (110) direction and a jump rate $1/\tau_1$.

Model (2): In extension to model (1) also jumps to second nearest neighbors are included. They occur in (100) direction across the cube face center with a jump rate $1/\tau_2$.

Model (3): Assumes that in addition to nearest-neighbor jumps correlated double jumps are possible. The corresponding jump rate is $1/\tau_2$.

Model (4): Generalizes model (3). It considers the H alternatively in a mobile "state" (life time τ), where it can perform repeated jumps to nearest neighbors with a jump rate $1/\tau_1$, and in an immobile self-trapped "state" (life time τ_t). The exchange between both "states" is described by transition rates given by the inverse life times. This concept is formal identi-

cal to the treatment of H diffusion in the presence of trapping impurities (40) which will be discussed later on.

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Fig. 6. Hydrogen sublattice for tetrahedral interstitial sites in bcc models.

Model (1) includes 2 independent parameters, the jump rate $1/\tau_1$ and the quasielastic intensity $I(Q)$, models (2) and (3) have 3 parameters and finally (4) is a four-parameter model. Fig. 7 shows the results of a data analysis applying model (1). While at room temperature, all spectra yield the same $1/\tau_1$, at higher temperatures severe deviations appear. The decrease of $1/\tau_1$ with increasing Q can be understood qualitatively as an increase of the effective jump length. Fig. 8 presents results obtained by an analysis of the high temperature data with the models (2) to (4). The jump rates calculated by a simultaneous fit of the spectra measured at different Q values for one crystal orientation ϕ are plotted vs ϕ . For a correct description of the data the obtained jump rates should not depend on the crystal direction. Fig. 8 makes it clear that the extension of model (1) to jumps to next-nearest neighbors does not solve the problem whereas the assumption of correlated jumps leads to a satisfactory agreement between theory and experiment. Similarly, also for H in Ta and V, the simple jump model (1) fails to explain the data at elevated temperatures, whereas model (3) seems to lead to an adequate description of the experimental results also for Ta and V. Model (4) has not been used

for the data analysis for Ta and V. However, the large ratio τ_1/τ_2 found for the contribution of double jumps makes the application of model (4) desirable.

Fig. 7. Jump rate $1/\tau_1$ of model (1) as a function of $|Q|$ determined from the measurements at 293 K, 431 K and 581 K (39).

The authors do not specify the physical origin of the occurrence of correlated jumps. Here the relation between the jump rate and lattice relaxation time τ_r , the time the lattice needs to dissipate the energy necessary to produce the jump, may be important. For the case of electronic small polaron hopping Emin has shown (41,42) that for times short compared to τ_r the energy required for a successive jump is only 1/3 of the activation energy in the relaxed lattice. However, the involved electronic hopping rates were in the order of 10^{14} sec^{-1} . In view of the much smaller jump rates of the proton $10^{12} - 10^{13} \text{ sec}^{-1}$ on the one hand and the differences in the coupling to the lattice on the other hand, it is not clear, whether this concept is applicable. Quantitative calculations are necessary.

Fig. 8. Jump rates as a function of sample orientation ϕ obtained by a simultaneous fit of the scattering law for the models (2), (3), (4), to the QNS result at 581 K (39).

The Q dependence of the quasielastic intensity evaluated from this experiment follows a normal Debye-Waller factor (DWF) behavior with mean-square amplitudes for the H-motion of $1/3\langle u^2 \rangle = 0.02 - 0.04 \text{ \AA}^2$ which is near to the value expected from harmonic calculations (27). For V an anomalous decrease of the intensity has been observed at larger Q values and high temperature ($T = 763 \text{ K}$) which was attributed to non-negligible jump times (27,39). The normal DWF evaluated for Nb and Ta even at high temperatures is in contrast to earlier reports of an anomalous behavior, which was mainly caused by errors in the integration of the quasielastic spectrum neglecting wing contributions. The observation of a normal DWF shows that the proton is well localized at its interstitial site contrary to earlier speculations about an extended proton wave function (25).

PHONONS AND H-DIFFUSION

During its rest time at a particular interstitial site the proton exhibits vibrational motion around its equilibrium position. Two types of motion have to be distinguished:

(i) localized vibrations of the dilute H-atom against its metal neighbor with frequencies typically a few times higher than the cutoff frequency of the host vibrations and

(ii) acoustic vibrations where the H follows the motions of the host atoms. These vibrational properties have been surveyed recently (43). Here we shall concentrate on features in the vibrational spectra which might be correlated to the diffusive motion of the proton.

Ultrasonic and neutron experiments reveal consistently an increase of the bulk modulus $(C_{11} + 2C_{12})/3$ and the shear modulus C_{44} in Nb, Ta (44, 51, 45). However, with respect to the shear modulus $C' = (C_{11} - C_{12})/2$ both techniques yield different results. In TaD_{0.02} a 12% increase of the phonon energies was found for the corresponding $(\xi, \xi, 0)$ T_{1A} branch, whereas from ultrasonic experiments ($\xi \approx 0$) a change of the phonon frequencies of less than 1% was observed. Similar observations were also reported for TaH_{0.18} (44, 45). From this, at small wave vectors, a H caused dispersion step in the $(\xi, \xi, 0)$ T_{1A} branch has to be assumed. In order to investigate whether this dispersion step is connected with the diffusive jump motion of the H-atom, the phonon frequencies in the region of the resonance condition $\omega\tau \sim 1$, were measured for NbH_{0.15} at 350 C where this condition is reached at $q \approx 0.08 \text{ \AA}^{-1}$ (4). The observed relative frequency shift $\Delta v/v = (v_{\text{NbH}_{0.15}} - v_{\text{Nb}})/v_{\text{Nb}}$ as a function of the reduced wave vector ξ is shown in Fig. 9. For $\xi > 0.1$ a constant value of $\Delta v/v = -0.7\%$ is observed, for $\xi < 0.1$ $\Delta v/v$ decreases, and reaches $\Delta v/v \sim -6\%$ at $\xi \approx 0.03$.

One is tempted to explain this behavior in terms of a relaxation process. The H-atom sitting on a tetrahedral site in the bcc lattice causes a tetragonal distortion field. A jump to a neighboring site turns this field by an angle of 90°. Such a rotation of the displacement field couples with the $(\xi, \xi, 0)$ T_{1A} mode in question. The sound velocity changes then from a relaxed behavior at low frequencies to unrelaxed behavior at higher frequencies. The solid line in Fig. 9 represents the theoretical curve for such a relaxation process.

$$\Delta v/v = A/(1 + (vq\tau)^2) + C \quad (8)$$

where v is the corresponding sound velocity. The position of the dispersion step is directly related to the jump time of the proton and its shape is well described by the above formula. However, this explanation contradicts other observations:

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Fig. 9. Relative shift $\Delta v/v = (v_{\text{NbH}} - v_{\text{Nb}})/v_{\text{Nb}}$ for TA_1 -phonons in (110) direction in $\text{NbH}_{0.15}$ at 350 C. The solid line represents the calculations based on Eq. (8) 4.

(i) diffuse neutron scattering experiments on NbD_x which probe the elastic distortion fields caused by the D reveal an essentially cubic displacement field (46).

(ii) internal friction experiments on bcc hydrides show the absence of the Snoek effect thereby supporting the view of a cubic displacement field (47).

(iii) the lack of a $1/T$ dependence of the step amplitude (44) points also in the direction that the relaxation process cannot be a normal Snoek effect. In conclusion, it is not understood how the long wavelength acoustic phonons can couple to the diffusive jump of the proton.

The acoustical and optical phonons in the bcc-H systems have been investigated thoroughly (43). Very recently, however, Shapiro et al. (5) reported the observation of new excitations in $\text{NbD}_{0.85}$ and $\text{NbH}_{0.82}$. Fig. 10 shows the dispersion curves measured along the three symmetry directions (1,0,0), (1,1,0) and (111) at $T = 160$ C in the liquid-like α' -phase of $\text{NbD}_{0.85}$. Included are also the dispersion curves in pure Nb (48) and pre-

Fig. 10. Dispersion curve for $\text{NbD}_{0.85}$ in the α' -phase at $T=160^\circ\text{C}$ and in the β phase at $T=20^\circ\text{C}$ (5) compound with results of $\text{NbD}_{0.45}$ (49) and those of pure Nb (48).

vious results on $\text{NbD}_{0.45}$ (49). The new features are the dispersionless excitations at 18.4 meV and at 10.8 meV. The positions of these frequencies do not depend on temperature nor do they change with isotope mass. The line width of the excitations broadens considerably in going from the ordered β phase to the α' -phase. In addition, the NbH system shows broader lines than the NbD sample. The authors argue against an explanation in terms of a density of state effect - in particular, there is no structure of the density of states in the 10 meV region - and against a defect mode; but they do not have a clearcut interpretation for the observed feature.

Thereafter, Lottner et al. (6) reported the observation of a strong peak at 15.7 meV in $\text{NbH}_{0.05}$ (Fig. 11). It appears at the position of the peak in the density of state for the transverse acoustic modes. The absence of a peak corresponding to the longitudinal cutoff frequencies (~ 23 meV) is against an explanation simply in terms of protons mirroring the acoustic phonons of the lattice. The authors propose an interpretation of this feature as a resonant-like mode of the protons within the acoustic modes of the Nb host. The local density of state

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Fig. 11. Energy spectrum for NbH_{0.05} curve 1:1-parameter model, curve 2:6 parameter model. The peak LA origins from the host lattice phonon (6).

for the H in the low frequency limit was calculated by standard Green-function techniques. Already the most simple approach using only one longitudinal coupling constant between the H and its nearest neighbors reveals a pronounced peak at 15.7 meV (curve 1 in Fig. 11). The H-atom vibrates with enhanced amplitude in phase with the surrounding host lattice atoms avoiding thereby a strain of the strong spring to the next-nearest neighbors. In a more sophisticated model, which describes more experimental data like the absence of Snoek effect and the change of the elastic constants, the calculations were repeated using now 6 parameters (curve 2 in Fig. 11). Although qualitatively the picture does not change, quantitatively, the intensity is even more enhanced. Because of the strong coupling of this resonant motion to the host lattice, only a very small isotope effect is expected (50). Whether the flat new modes, found by Shapiro et al. (5) in the high concentration regime, can be interpreted in the same way, is an open question.

THE INFLUENCE OF DEFECTS ON H-DIFFUSION

Numerous investigations have demonstrated that the physical properties of H dissolved in bcc-transition metals are strongly changed by the presence of small amounts of impurities. Vapor pressure data show deviations from Sieverts law at low concentrations which increase by introducing oxygen impurities into Ta or due to cold working of V (51,52). Solubility data reveal a shift of the phase boundary between the α - and β -phase in the presence of O-, N or C-impurities (53). Applying very low cooling rates in Ta-H the phase boundary of the pure material is observed (54) whereas in Nb-N (55) a shift independent of the cooling rate is found. Resistivity experiments on Nb-H doped with N (55) yield a reduced residual H-resistivity at temperatures well above the phase boundary to the β -phase. Furthermore, Gorsky-effect measurements in NbN_xH_y samples (56) showed a strong decrease of the H-diffusion coefficient in particular at lower temperatures. Finally, in the presence of O- and N-impurities in the Nb-H system additional relaxation peaks in internal friction experiments are observed (57). All these features are naturally explained in terms of H trapping at the impurities. In their vicinity they lower the ground state energy for the H. This gives rise to deviations from the Sieverts law at low concentrations due to an increase of the enthalpie of solution. If the binding energy at the trapping center is larger than the enthalpie of formation for the ordered β -phase, the solubility in the dilute phase increases. Resistivity measurements suggest that in NbN each N-impurity is capable of keeping one H from precipitating into the β -phase, whereas in TaH oxygen impurities do not prevent precipitation. Trapping implies the formation of impurity hydrogen pairs. They are assumed to scatter conduction electrons with a smaller probability than the two single scattering centers and they give rise to relaxation processes in internal fraction experiments. Their results will be treated in more detail in the next chapter. Such trapping processes also slow down the long range diffusion. The significance of the trapping processes will increase with increasing ratio of binding energy and thermal energy kT .

On a microscopic level, the influence of interstitial impurities on the H-diffusion process was studied recently by quasielastic neutron scattering on Nb-H samples doped with nitrogen impurities (7). The trapping capability of substitutional defects was investigated for the Nb-V-H system by means of NMR (58). For this system also preliminary neutron scattering results are available (59). Both will be discussed in the following section.

For low concentrations of trapping impurities, where trapping regions and regions of undisturbed host material are present, relatively simple arguments can be given, in order to explain what kind of information can be obtained from a quasielastic neutron scattering experiment. For small momentum transfers, the scattering process averages over large volumes in space (of the order $(2\pi/Q)^3$). Therefore, a long section of the diffusive path of the proton will be probed by the neutron wave packet. This path consists out of periods of undisturbed diffusion as well as of portions where the proton is trapped. Under these circumstances, the scattering law is expected to be a single Lorentzian whose width is given by the effective or macroscopic H-diffusion coefficient D_{eff} in the system. At large Q 's, however, the average occurs over short distances and the scattering law depends on the single diffusive step. In this case, the scattering law contains information about the mean trapping time and on the fraction of protons being trapped.

Quantitatively, the scattering law has been calculated in terms of a phenomenological two-state random walk model (RWM) thereby approximating the complicated structure of the trapping region around the impurity by a single escape rate $1/\tau_0$. This approach was confirmed later using the average T-matrix approximation in the limit of dilute concentration of traps (60). We shall survey briefly the RWM approach. Here it is assumed that the proton diffuses in a crystal with randomly distributed traps. The proton diffuses e.g. through the undisturbed parts of the lattice for an average time τ_1 exhibiting jumps with the jump rate of the undisturbed lattice $1/\tau$. Thereafter, it is trapped at the impurity for an average time τ_0 . Thus $1/\tau_1$ is the trapping rate and $1/\tau_0$ the escape rate. The self-correlation function is easily calculated using the self-correlation functions of the proton in the undisturbed lattice and in the trapped state. The mathematical procedure is outlined in detail in Ref. (7). The result for the incoherent scattering law is a superposition of two Lorentzians with width Λ_1 and Λ_2 and weights R_1 and R_2 . $\Lambda(Q)$ is the line width in the undisturbed lattice.

$$S_{\text{inc}}(Q, \omega) = R_1 \frac{\Lambda_1/\pi}{\Lambda_1^2 + \omega^2} + R_2 \frac{\Lambda_2/\pi}{\Lambda_2^2 + \omega^2} \quad (9)$$

$$\Lambda_{1/2} = \frac{1}{2} \left(\tau_0^{-1} + \tau_1^{-1} + \Lambda(Q) \pm \left(\tau_0^{-1} + \tau_1^{-1} + \Lambda(Q) \right)^2 - 4\Lambda(Q)/\tau_0 \right)^{1/2}$$

$$R_1 = \frac{1}{2} + \frac{1}{2} (\Lambda(Q) \frac{\tau_1 - \tau_0}{\tau_1 + \tau_0} - \tau_1^{-1} \tau_0^{-1}) / (\tau_1^{-1} + \tau_0^{-1} + \Lambda(Q))^2 - 4\Lambda(Q)/\tau_0^{-1})^{1/2} \quad (10)$$

$$R_2 = 1 - R_1 \quad (11)$$

The typical properties of the scattering law are shown in Fig. 12, where the widths Λ_1 and Λ_2 of the two components are plotted together with their weights vs. DQ^2 . Included also is $\Lambda(Q)$ of the undisturbed lattice. For the sake of simplicity the calculations are made for a simple cubic lattice. Using the average T-matrix approach, explicit expressions for $1/\tau_1$ and $1/\tau_0$ were found (60). The leading term of the escape rate $1/\tau_0$ is independent of the trap concentration whereas the trapping rate $1/\tau_1$ is proportional to the concentration as expected.

Quasielastic neutron scattering experiments were carried out on Nb samples doped with N and H. The N-concentrations were $C_N^1 = 0.7\%$ and $C_N^2 = 0.4\%$. The corresponding H concentrations were $C_H^1 = 0.4\%$ and $C_H^2 = 0.3\%$. The experiments have been performed in a temperature range $180 \leq T \leq 373$ K for $0.1 \leq Q \leq 1.9$ $\text{\AA}^{-1}$. The measurements were made, using the high-resolution back-scattering spectrometer at the ILL Grenoble. The energy resolution (FWHM) was between 0.7 and 1.5 μeV the scanning range $\Delta E = \pm 5.3$ eV. As a consequence of the small value of ΔE , at larger Q's only the narrow component could be measured. The integrated intensity of the quasielastic line, as observed within ΔE , as a function of Q and the temperature is shown in Fig. 13. The intensity has been normalized to the total intensity I obtained at 73 K. For small Q nearly the full intensity is concentrated within the energy window. This demonstrates the existence of only one line which falls entirely within the instrumental energy range. However, at larger Q's, only a fraction of the intensity appears in the integration window which decreases with increasing temperatures. This behavior reflects the reduction of the trapped fraction of protons with the temperature. The experimental spectra for $Q \leq 0.9$ $\text{\AA}^{-1}$ below) were fitted with the scattering law of the RWM, τ_0 and τ_1 being the only disposable parameters. The result is presented in Fig. 14. Compared to typical jump rates τ^{-1} of 10^{+11} jump/sec τ_0 and τ_1 are two orders of magnitude smaller. At higher temperatures $\tau_1 > \tau_0$ holds; the protons are mainly in undisturbed regions. At lower temperatures, we have $\tau_1 < \tau_0$, the protons are predominantly trapped. τ_0 as a local property of the traps does not depend on the N-concentration justifying the assumption of well-separated trapping and undisturbed regions in the lattice. From the activation energy of $1/\tau_0$ (166

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Fig. 12. Line width of the two components Λ_1 and Λ_2 , (solid lines) and their spectral weights (dashed lines) R_1 , R_2 in the scattering law for the RWM description of diffusion in the presence of traps. Dashed dotted line: line width for an undisturbed lattice (7).

meV) a binding energy of approximately 100 meV for the N-H pair can be deduced. The capture rate $1/\tau_1$ depends on the N-concentration. The ratio of $1/\tau_1$ for the two N-concentrations of 1.8 ± 0.2 compared to the ratio of N-concentrations of 1.9 ± 0.2 is in agreement with theory (60). According to the average T-matrix approximation as well as to results of simple reaction theory for trapping (61) which yields

$$1/\tau_1 = 4\pi R_t D c_t \quad (12)$$

where R_t is the trapping radius and C_t is the trap concentration, the activation energy for $1/\tau_1$ should agree with the activation energy for the self-diffusion coefficient D . The resulting higher values (94 meV) can be explained by the assumption that the nitrogen impurities are saturated as soon as they have trapped a single hydrogen (see also Ref. 55). After correction for saturation effects Eq. (12) allows the evaluation

Fig. 13. Intensity of the observed quasielastic spectrum at the $\text{NbN}_{0.007}\text{H}_{0.004}$ -sample within the energy window $\pm\Delta E$ as a function of inverse temperature for different Q . The intensity is normalized to the total intensity determined at 73 K (7).

of the trapping radius R_t . Values in the order of $5 \text{ \AA}$ result which are in good agreement with calculations using anisotropic continuum theory. Furthermore, the mean-free path between two trapping events can be calculated. It decreases with increasing temperature demonstrating the saturation effects of the traps. Its absolute value is slightly larger than the mean distance between the nitrogen impurities. Summarizing, the simple two-state RWM represents the experimental results below $Q = 0.9 \text{ \AA}^{-1}$ very well. It has been shown that it is also applicable to muon diffusion in the presence of traps (62). Also problems of chemical reactions implying hydrogen atoms might be treated with such a model.

At large Q values a direct determination of the escape rate $1/\tau_0$ should be possible. Fig. 15 presents the width of the narrow components of the quasielastic line for two larger Q values. The activation energy of an Arrhenius law for $\Gamma(T)$ at $Q \approx 1.9 \text{ \AA}^{-1}$ is only 115 meV, compared with the expected value of ~ 170 meV. Thus the connection between $\Gamma(T)$ and the escape process is more intricate than expected. It is obvious that the detailed structure of the disturbed region around a nitrogen interstitial affects the scattering law at larger Q . Thus, a model has been investigated which takes into account the lattice distortions created by the nitrogen interstitials (63). The nitrogen atoms were located at tetrahedral sites in a niobium lattice. The

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Fig. 14. Escape rate $1/\tau_0$ and trapping rate $1/\tau_1$ as a function of inverse temperature and nitrogen temperature. For $1/\tau_0$: Δ : $C_N = 0.7\%$, $x = C_N = 0.4\%$ (7).

lattice distortion was calculated from the Kanzaki forces of the nitrogen atoms, fitted to lattice expansion and Snoek effect measurements, and from the niobium force constants, determined from phonon spectra. The equilibrium energies were determined from the lattice distortion and the Kanzaki forces of a proton. The potential maxima were assumed to be equal. Electronic contributions to the hydrogen-nitrogen interaction were approximated by a hard-core potential. The self-correlation function for diffusion of a proton $G_s(\underline{r}, t)$ was calculated by numerically solving the rate equations. A cube with 16 000 niobium atoms and 128 nitrogen atoms was used. The results for D_{eff} and the width Γ of the narrow component for large Q are shown in Fig. 5 as two lines. One obtains good agreement between the calculations and the experimental points for D_{eff} and Γ . Especially the activation energy of Γ was found to be similar to the experimental one. This relatively low activation energy can be understood from the combined effect of different small jump rates near the trap (64).

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Fig. 15. Effective diffusion constant (lower left part) and width Γ of the quasielastic spectrum for two Q -values (upper right part) as a function of inverse temperature. The lines are the result of the numerical calculations (63).

The influence of substitutional defects on H-diffusion in Nb has been investigated recently by NMR (58) and later by quasielastic neutron scattering (59). The NMR experiments have been performed on $\text{Nb}_{1-x}\text{V}_x\text{H}_y$ - powder samples ($x = 0.05$ and 0.08) with varying H concentrations C_H . Investigated were: (i) the line width Γ_{Nb} of the Nb^{93} absorption line as a function of H concentration. The observed line width decreases sharply with increasing H-concentration. At the hydrogen concentration, where C_H reaches the vanadium concentration C_V , a break in the concentration dependence of Γ_{Nb} occurs which leads to a weak dependence of Γ_{Nb} or C_H for $C_H > C_V$. (ii) the hydrogen line width Γ_H as a function of temperature. In the temperature region $150 < T < 200$ K Γ_H decreases to its high temperature value which does not change up to 310 K, the highest temperature investigated. This result does not depend on the H-concentration. (iii) the Knight shift at the V nucleus as a function of H-concentration and temperature. Fig. 16 shows the observed sharp

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Fig. 16. ^{51}V Knight shift as a function of H-concentration in (a) $\text{Nb}_{0.095}\text{V}_{0.05}\text{H}_x$ and (b) $\text{Nb}_{0.92}\text{V}_{0.08}\text{H}_x$ systems at room temperature. The dotted line shows the solubility limit of hydrogen in the $\text{Nb}_{0.55}\text{V}_{0.05}$ -alloy (58).

increase in the Knight shift K_V for $C_H/C_V < 1$. At $C_V = C_H$ again a break in the concentration dependence is observed. For $C_H > C_V$ K_V depends only weakly on C_H . Both the Knight shifts K_V in a H-free $\text{Nb}_{1-x}\text{V}_x$ sample and in $\text{Nb}_{1-x}\text{V}_x\text{H}_y$ increase with temperature. However, the rate of increase observed for the H-containing sample is much weaker than in the H-free sample.

All these results have been interpreted in terms of H-trapping at the V substitutional atom. The large Nb line width in $\text{Nb}_{1-x}\text{V}_x$ can be understood as a result of second order quadrupolar interaction. The V-atoms introduce internal strains which create an electric field gradient acting on the Nb nuclei. The sharp decrease of line width with increasing H concentration was attributed to a relaxation of the internal strains by the dissolved H atoms. In this picture V-H pair formation compensates for the lattice deformation caused by the small V-atom (atomic radius r_V 8.5% smaller than r_{Nb}). The observed com-

plete motional narrowing of the proton line for temperatures $T > 200$ K independent of C_H led to the assumption of high H mobility near the V impurity. Fig. 6 shows that around a substitutional V-atom, which can be assumed to sit in the center of the cube, are 24 equivalent tetrahedral H sites. Rapid motion between these sites does not require a dissociation of the pair and can account for a similar line narrowing as observed for free H atoms.

Already earlier Knight-shift experiments (65) on VH_x compounds have shown an increase of K_V with increasing H concentration. This has been interpreted in terms of a H-atom donating its electron to the conduction band. Thereby the increase of K_V is due to the decrease of the negative core polarization contribution, K_C . K_C is related to the d-density of states at the Fermi energy, which decreases with increasing H concentration. The rate of increase in K_V above $C_H/C_V = 1$ is in accordance with the results found in the earlier measure measurements on VH_x . For $C_H/C_V < 1$, however, the increase in K_V is considerably larger than at higher concentrations. This has been attributed to a local change in the electronic structure at the V-nucleus due to V-H pair formation. Assuming that the electron of the hydrogen forming the pair contributes only locally to the change of the electron density in the d-states, a consistent description of the results on VH_y and $Nb_{1-x}V_xH_y$ evolves. In this picture a V-H pair gives rise to a local H concentration of 25% (1 H atom/4 surrounding atoms). The observed Knight shift corresponds to the value obtained in $VH_{0.25}$. The temperature dependence of the Knight shift provides information on the thermal occupation of the trapping sites. The weaker increase of the Knight shift with temperature compared to H-free $Nb_{1-x}V_x$ is then a consequence of the partial decomposition of the V-H pairs with increasing temperature. This tends to diminish the temperature effect on K_V . A quantitative evaluation of the binding energy yields $E_b = 90 \pm 50$ meV.

Again, quasielastic neutron scattering could provide direct insight into the trapping mechanism as well as in the dynamics of the protons in the trapped state. Preliminary results on $NbV_{0.002}H_{0.004}$ have been reported (59). The quasielastic spectra were measured in the temperature region $178K \leq T \leq 247K$ for Q 's $0.13 < Q \leq 1.8 \text{ \AA}^{-1}$. Fig. 17 shows the width Γ of the spectra for the two smallest Q -values as a function of inverse temperature. Assuming that in this Q -range the line width is still proportional to the effective H-diffusion coefficient of the system, D_{eff} was evaluated. For comparison, the temperature dependence of the line width for a pure Nb sample (16) is indicated as a dashed line. In the next step of data refinement, all spectra with $Q \leq 1 \text{ \AA}^{-1}$ (see above) were fitted

Fig. 17. Quasielastic line width of H in $\text{NbV}_{0.002}\text{H}_{0.004}$ at small Q 's. Dashed line expected line width for a pure NbH-sample (59).

simultaneously with the scattering law of the RWM (Eq. (8)). Thereby an exponential temperature dependence of the two rates τ_0^{-1} and τ_1^{-1} was assumed. The activation energy for τ_1^{-1} was taken equal to the energy of migration in the undisturbed lattice (68 meV). Under these circumstances, the fitting process yields an activation energy for τ_0^{-1} of $E_a = 163 \pm 10$ meV. From E_a a binding energy $E_b = 95 \pm 10$ meV can be derived. This value is in agreement with the Knight shift result. The evaluated prefactor for $1/\tau_1$ of $\tau^{-1} = (3.6 \pm 0.3) \times 10^{-10}$ sec corresponds to a trapping radius of $R_t = 3.2$ Å. Due to the very low impurity concentration, however, this experiment did not yield information on the local dynamics at the trap.

DYNAMICS OF THE H-ATOM TRAPPED AT AN IMPURITY ATOM

In order to explain the observed concentration independent motional narrowing of the NMR-proton line in $\text{Nb}_{1-x}\text{V}_x\text{H}_y$, rapid H-motion around the substitutional V-atom had to be assumed (58). However, nothing is known about details of this motion. In contrast to the situation at substitutional impurities a larger number of experiments on the dynamics of the proton in the

vicinity of an interstitial impurity like oxygen or nitrogen in Nb are available (8,57,9).

Already early experiments revealed a low temperature internal friction peak in Nb-H systems which was ascribed to H and D Snoek relaxations (66). Later Baker and Birnbaum (57) showed that these peaks only appear in the presence of O and N impurities in Nb. Consequently, they were explained by a reorientational relaxation of the O-H or N-H pairs. For a temperature independent concentration of defects the condition of maximum internal friction is fulfilled for $\omega\tau = 1$, where ω is the incident frequency of the acoustic wave and τ is the relaxation time of the system. Thus varying the temperature at different frequencies allows a determination of the temperature dependence of the relaxation time. The relaxation strength Δ is proportional to the number of relaxing species. Therefore, the temperature dependence of Δ yields information on the binding energy at the trap. Baker and Birnbaum found relaxation rates τ which changed with the impurity concentration. This concentration dependence was attributed to a possible super position of different relaxation processes caused by N-H or O-H pairs (the O/N ratio varied with sample purity). The evaluated parameters for the relaxation rate and the binding energy are shown in Table III. More recently these experiments have been repeated and extended on better characterized samples using H as well as D (67). Single crystalline UHV purified Nb-samples were doped with controlled amounts of O and H or D. The experiments were carried out in the temperature range 80-350 K and in the frequency range 30-210 MHz. The longitudinal wave propagation direction was (100). The most interesting feature of these measurements is the pronounced isotope effect in the H-relaxation as well as in the binding energy of the O-H pair. The resulting parameters for the relaxation rate and the binding energy are shown in Table III.

A detailed site occupancy of the O-H pair has not yet been established (channeling experiments on NbO_xH_y samples are underway (68). However, the coupling of the longitudinal acoustic wave in (100) direction with the strain field of the pair requires a (100) pair symmetry. Octahedral sites for the O as well as for the H have been proposed but also tetrahedral site occupancy is possible for this symmetry. On the other hand, also a (111) pair symmetry for the O-H pair has been reported (69). Various mechanisms for the reorientation process, which involve partial dissociation of the pair, have been discussed. But, as long as the actual position of the proton is not known those discussions remain speculative. Also, the large isotope effect in the relaxation rate as well as in the binding energy is not understood. From the absence of an isotope effect in the

double-force tensor for H and D in Nb similar binding energies for both species are expected in the framework of elastic theory. The ratio of H and D jump frequencies is far away from the prediction of the classical jump theory $\tau_D/\tau_H = \sqrt{M_D/M_H} = \sqrt{2}$ ($\tau_D/\tau_H(260K) = 2.3$; $\tau_D/\tau_H(100K) \approx 200$). Also the tunneling hopping theory in its simplest form (24) cannot account for the observed isotope dependence. It would predict a large isotope effect in the prefactor due to the smaller tunneling matrix element for D and no isotope effect in the activation energy due to the absence of isotope effect in the double-force tensor for D and H.

Table III. Relaxation rates $\tau^{-1} = \tau_0^{-1} \exp(-E/kT)$ and binding energies for O-H and O-D pairs in Nb.

Defect	$\tau_0^{-1}(s^{-1})$	E(meV)	E_B (meV)
O-H (57) (low purity)	$(7.3 \pm 5) 10^{11}$	170 ± 25	90 ± 25
O-H (7) (int. purity)	$(8 \pm 10) \pm 10^{12}$	165 ± 25	---
O-H (8)	$1.3^{+1.2}_{-0.4} 10^{12}$	160 ± 10	90 ± 10
O-H (8)	$2.5^{+2.5}_{-0.8} 10^{12}$	200 ± 20	130 ± 20

Recently, the internal friction measurements on O-H(N-H) pairs in Nb were extended to low temperatures and long relaxation rates (8). Strain relaxation experiments allowed to monitor jump rates down to 10^{-3} Hz. The experiments were performed on U.H.V. purified polycrystalline Nb samples doped with controlled amounts of O or N. The observed relaxation frequencies were equal for H-N and H-O clusters. Fig. 18 presents the observed relaxation frequencies as a function of inverse temperature. Included are results from earlier experiments at higher temperatures. Fig. 18 clearly shows strong deviations from an Arrhenius behavior at low temperatures. The authors attributed this behavior to a tunneling hopping process of the proton around the impurity. The data were fitted with the expression of the small polaron theory for the jump rate in Debye approximation (25) (dashed line in Fig. 18). It depends on three

Fig. 18. The logarithm of the hopping frequency of H around a O impurity vs $1/T$. O Mattas (67) □ Schiller (69), o Chen (8), Δ Canelli (66).

independent parameters: the distortion energy necessary to equalize adjacent potential wells, the Debye temperature θ_D and the tunneling matrix element J . They were evaluated to: $E_a = 211$ meV, $J = 53.4$ meV and $\theta_D = 263.6$ K. However, considering the presumable multistep reorientation mechanism involving partial dissociation in a highly distorted lattice near the impurity (67), the application of the tunneling hopping theory in its simplest form seems not to be adequate for the problem, as already demonstrated by its failure to explain the isotope effect for the reorientation rate. Therefore the resulting parameters might not have a direct physical meaning, e.g. a value in the order of 200 meV for E_a would imply an extraordinary deep potential well due to polaron formation. This has to be compared with an expected value of 26 meV calculated by Wagner and Horner (70) for pure Nb on the basis of elastic lattice theory.

A few years ago, Sellers et al. (71) reported the observation of a low temperature specific heat anomaly in Nb. The strong isotope effect made it clear, that the observed feature was caused by the H or D atoms. Birnbaum et al. (72) ascribed this phenomenon to proton tunneling among tetrahedral and triangular interstices on a cubic face within a polaron like distorted lattice region. Very recently the relation between the specific heat anomaly and the presence of N-impurities in Nb has been investigated systematically (9). The specific heat of UHV purified Nb, Nb doped with N or H and Nb doped with N and H or D was measured in the temperature region 0.07 - 1.5 K. Fig. 19 shows the obtained specific heat data together with the results reported by Sellers et al. They clearly demonstrate (i) that pure Nb as well as Nb doped either with H or with N exhibit essentially the same low temperature behavior which is very close to the expected calculated curve*; (ii) that samples containing both N and H or D show a large isotope dependent specific heat anomaly. Thus, the anomaly is related to the presence of both the N-impurity and the H-atom which at the low temperatures in question is trapped at the impurity. From the reported low residual resistivity ratio (100) it can be concluded that Sellers et al. already observed the same phenomenon. Because nothing is known about the geometry of the N-H pair, however, it is impossible to calculate the specific heat anomaly and the underlying system of tunneling levels. Also a correlation between the specific heat anomaly and the low temperature relaxation mechanism observed with internal friction is not obvious. The time scale of motion for both processes differs by more than 10 orders of magnitude (10^{-3} Hz and $35 \text{ K } 10^{+11} \text{ s}^{-1}$ at 1 K). Therefore, even a knowledge of the sites involved in the relaxation mechanism would not provide necessarily the geometry of the tunneling process. In this connection the authors speculate about (i) additional low energy sites around a nitrogen atom which are populated at low temperatures and (ii) that the reorientation in internal friction might occur between systems of tunnel split sites. The relatively low size of the anomaly (entropy increase due to the specific heat anomaly is only 0.055 k_B and 0.087 k_B per trapped H and D respectively) was attributed to stress induced interaction effects among neighboring N-H pairs. On the basis of elastic continuum theory the potential disturbance due to the neighboring defects was estimated to $\approx 1 \text{ meV}$ in the average which is larger than the thermal energy of the anomaly. Their influence on the experimental result, therefore, is quite understandable. These blocking effects are also the reason that neutron scattering experiments, performed to reveal detailed microscopic information on the tunneling process, have been unsuccessful so far (73).

*for pure Nb.

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Fig. 19. Specific heat of Nb-samples partially doped with H,D and N in a log-log plot. $\circ$ pure Nb, $\square$ NbN_{0.003}, Δ NbH_{0.002}, $\diamond$ NbN_{0.006}, $\triangle$ NbN_{0.003} D_{0.002}. The solid lines are guide lines for the eye. The dashed line represents the results of Sellers et al. (71). The dashed pointed line gives the calculated specific heat for pure Nb (9).

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Note added in proof

A reinvestigation of the "new excitations" in NbD_{0.85} has shown that the 10.8 meV feature is a false peak. The 18.9 meV remains real.

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