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A ^{2}D NMR study of deuterium trapping by dislocations in palladium

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Abstract. Deuteron spin–lattice and spin–spin relaxation rates have been measured in annealed and cold-rolled foil samples of palladium deuteride $PdD_{\approx 0.6}$ in the temperature range 100–390 K using pulsed NMR at 14.8 MHz. The CPMG sequence spin–spin decay in samples containing different densities confirms the coexistence of two relaxation rates, $R_{2a} < R_{2b}$ (≈ 11 and $\approx 170\ s^{-1}$ at room temperature for instance), both of which are much larger than R_1 ($\leqslant 0.42\ s^{-1}$). R_{2a} describes relaxation of deuterons in normal interstitial sites whereas R_{2b} is thought to originate from deuterons trapped in dislocation core regions. For $T \leqslant 160$ K, R_1 and R_{2a} are attributed to a diffusion-modulated, deuterium-vacancy-induced, quadrupolar interaction; for $T \geqslant 160$ K, R_{2a} is dominated by quadrupolar interactions of diffusing deuterons with long-range electric field gradients associated with dislocation strain fields. The temperature dependence of R_{2b} yields an activation energy of ≈ 0.024 eV for deuterium diffusion within the core regions where a quadrupolar coupling constant of at least 4 kHz is measured. In spite of this low activation energy, diffusion in the cores is relatively slow since nearly all sites in core regions are filled. It is estimated from the signal amplitudes that trapping can cause almost all dilated deuterium sites to be filled out to a radius of 30 Å around dislocation cores for a dislocation density $\sim 10^{12}\ cm^{-2}$.

1. Introduction

The dislocation–hydrogen interaction in metal–hydrogen systems including Pd–H has been investigated by several techniques which include internal friction (Bordoni 1986), resistivity (Rodrigues and Kirchheim 1983), electrochemical (Kirchheim 1981), tritium tracer (Sicking *et al* 1983), x-ray diffraction (Balbaa *et al* 1987), neutron scattering (Carstanjen *et al* 1989) and nuclear magnetic resonance (NMR) (Messer *et al* 1986) experiments. Hydrogen and its isotopes (as well as other light impurities) are known to segregate at the core of dislocations (Cottrell atmospheres) where sites with deeper potential energy wells are available.

The NMR technique offers a convenient method for detecting the presence and probing the motion of hydrogen in the vicinity of dislocations. Some twenty years ago, Gil'manov *et al* (Gil'manov and Bikchantayev 1970, Gil'manov and Fedotov 1971) observed the coexistence in samples of α'-PdH_x of two ^{1}H NMR spin–spin relaxation rates, R_{2a} and R_{2b}, one of which, R_{2b}, was faster than the observed spin–lattice relaxation rate R_1. They ascribed R_{2a} and R_{2b} to the presence of two non-equivalent sites *a* and *b* for protons having slightly different resonance frequencies. R_1 and R_{2a} were equal at high temperatures and were attributed to nuclear magnetic dipole–dipole interactions

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and interaction with conduction electrons, for mobile protons in normal octahedral sites. They were unable to positively identify the origin of R_{2b}, but subsequent work (Holley *et al* 1983), to be discussed below, suggests that R_{2b} is associated with less-mobile protons in dislocation cores.

Dislocations are known to produce long-range strain fields (r^{-1} dependence) which result in long-range electric field gradients (EFGs) around dislocation lines. It may therefore be an advantage to use quadrupolar nuclei, such as deuterons, which can interact with these EFGs leading to an additional contribution to relaxation. ^{2}D NMR in metal deuterides therefore allows an investigation of both long-range and short-range distortions due to dislocations. The investigation by Holley *et al* (1983) on samples of α'-PdD$_x$ prepared by passage through the α–α' mixed-phase region of the phase diagram has also revealed two coexisting relaxation rates R_{2a} and R_{2b} for ^{2}D. Since they observed only a single rate equal to R_{2a} in samples prepared by a method that avoided the mixed region, they tentatively identified sites b with extended cores of dislocations which are known to be generated accidentally by the former sample treatment. In the following we show how a controlled generation of deformations in the lattice leads to a systematic change of the NMR parameters in palladium deuteride. This work at high concentrations (α'-phase) of deuterium complements earlier investigations of nuclear spin relaxation at low concentrations of hydrogen by Messer *et al* (1986), on niobium and tantalum, and Pfiz *et al* (1989) on NbH$_{0.02}$.

2. Experimental procedure

Pieces of 99.98% purity palladium foils 25 μm thick or less were cleaned with carbon tetrachloride and annealed under vacuum at 800 °C. The samples were exposed at 400 °C to deuterium gas (99.7 at.% pure) at a pressure of 36–40 bar. They were then cooled gradually at constant pressure, thus avoiding the mixed-phase region and ensuring the generation of a minimum number of dislocations. After measurements of R_1 and R_2 had been performed on this annealed α'-PdD$_{0.68\pm0.03}$ specimen (sample I), the same foils were cold-rolled, producing a linear extension of $\simeq 6\%$, to generate dislocations. Measurements of R_1 and R_2 were carried out on this cold-worked sample (sample II); after further cold-working to an extension of $\simeq 17\%$ (sample III) R_2 was again measured.

All the measurements were performed at 14.8 MHz using a pulsed NMR spectrometer. The RF magnetic field produced in the coil was about 38 G for a typical deuteron 90°-pulse. R_1 was measured using the inversion–recovery sequence with a repetition time of at least 15 s chosen because of the comparatively long spin–lattice relaxation time. R_2 was measured using the Carr–Purcell–Meiboom–Gill (CPMG) sequence (see, for instance, Cotts 1978) where a maximum of 128 180°-pulses allowed the sampling of the transverse relaxation.

3. Results and discussion

3.1. Spin–lattice relaxation

^{2}D spin–lattice relaxation rates R_1 were measured over the temperature range 160–340 K for the annealed sample. A maximum in R_1 was observed at $\simeq 222$ K. If this is attributed to diffusion-controlled modulation of the quadrupolar fields at deuteron sites, then (after subtraction of small nuclear dipolar and conduction electron contributions) a value of the quadrupolar coupling constant $\nu_Q^v = (2.4 \pm 0.1)$ kHz was deduced. This value is comparable with that obtained by Bogdan *et al* (1979) (2.6 kHz) and Holley *et al* (1983) (~1 kHz). However, the variation of R_1 with $1/T$ away from the maximum yields an activation energy for diffusion that is three times smaller that the previously observed value of ≃0.21 eV. We suspect therefore that a non-negligible contribution to relaxation is provided by paramagnetic impurities and that this distorts the slope and changes the value of the maximum. If this is the case, the value for ν_Q^v should be reduced but it is difficult to estimate by what factor. (Spin–spin and spin–lattice relaxations due to paramagnetic centres are expected to be comparable (<1 s^{-1}), so there is a negligible effect on our measurements of R_2 since R_2 is much larger than this. The same is true for relaxation produced by conduction electrons ($T_{1e}T \simeq 3500$ s K). For these reasons, most of the information deduced in this work comes from R_2 rather than R_1.) Measurements of R_1 on sample II at 294 K and 202 K gave results equal to those for sample I within experimental error showing that R_1 is essentially unaffected by the presence of dislocations. The origin of the quadrupolar coupling responsible for the majority of the quadrupolar contribution to R_1 must therefore be the random arrangement of vacant octahedral deuterium sites in this substoichiometric deuteride, in the bulk of the material (i.e. not connected with dislocation cores) (Barton and Seymour 1985). However, experiments over a wider temperature range, at very much lower concentrations of *hydrogen and in more deformed samples have revealed a spin–lattice process attributable* to pipe diffusion along dislocation lines (the Γ_1' process in Pfiz *et al* 1989). We believe that the essential difference in those experiments was that pipe diffusion in the low-concentration α-phase investigated was not blocked by near-complete occupation of interstitial sites within the cores, and was therefore rapid enough to produce significant spin–lattice relaxation; almost complete site-blocking prevents this in the present samples, except at inaccessibly high temperatures.

3.2. *Spin–spin relaxation*

An example of a transverse magnetization decay produced by the CPMG sequence is shown in figure 1. The data points, which represent the integrated spin-echo signals, reveal the existence of two decays in the annealed and in both cold-worked samples. (Coexistence of two decays is not peculiar to PdD_x: we have observed similar effects in substoichiometric TiD_2.) The two decays are well fitted by exponential functions of time. Exponential decays are indeed to be expected in all motionally narrowed situations, which applies to the majority of our measurements.

The two decays originated from deuterons dephasing in two distinct sites. The slower rate R_{2a} is attributed to deuterons free to move in the normal (essentially undeformed) lattice whereas the faster rate R_{2b} is attributed to deuterons trapped in the immediate vicinity of dislocations. The just-observable, small-amplitude beat (between 10 ms and 30 ms in figure 1) between the two decays in the CPMG sequence is thought to indicate slightly different Knight shifts (≃3 ppm) for the two types of site. This is reasonable since it corresponds to a significant fraction (≃15%) of the bulk shift (see Bowman 1985), which can readily be caused by conduction electron density and/or density of states disturbances within the cores. Contrary to the work of Holley *et al* (1983), we observe a short component even in the 'annealed' sample suggesting that our polycrystalline foil contains already a non-negligible residual density of dislocations.

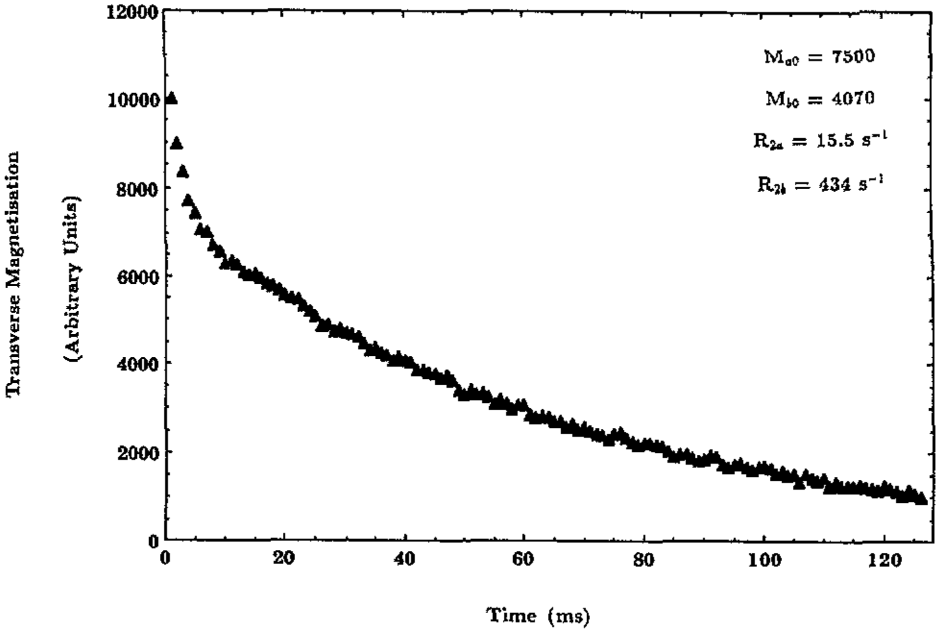

Figure 1. Deutron magnetisation decay in PdD$_{\approx 0.68}$ at 215 K given by the CPMG sequence and showing a double exponential decay $M_{a0}\,e^{-R_{2a}t} + M_{b0}\,e^{-R_{2b}t}$ ($R_{2a} < R_{2b}$).

The two relaxation rates R_{2a} and R_{2b} together with the ratio of the initial amplitudes of the two component decays were extracted from the CPMG data points using a non-linear least-squares fitting procedure and recorded as a function of temperature (100–350 K) in all samples.

3.2.1. Temperature dependence of R_{2a}: untrapped deuterium. The slower spin–spin relaxation rate R_{2a} is plotted in figure 2 as a function of inverse temperature $1/T$ for samples I, II and III.

This rate shows a systematic increase with amount of cold-working at all temperatures. We also note a sharp rise of R_{2a} with falling T in all the samples below about 160 K. This behaviour may be explained, as suggested by Cotts (1978) and Seymour (1982), by the existence of two quadrupolar interactions from different sources, $R_{2a} = R_{2a}^{v} + R_{2a}^{d}$, each modulated with its own correlation time. (Superscripts v and d will be used throughout to denote quantities related to vacancies and dislocations, respectively). R_{2a}^{v} represents the interaction of quadrupole moments of deuterons with EFGs produced by neighbouring hopping deuterium ions (or equivalently, by deuterium vacancies). R_{2a}^{d} is also due to quadrupolar relaxation but EFGs are now produced by the long-range strain fields of dislocations which are associated with a longer correlation time than for the short-range interaction, since the correlation time represents the average time taken for an ion to diffuse over a distance for which the interaction changes appreciably in magnitude: a lattice constant in the one case, and roughly the separation of dislocations in the other. The decrease of R_{2a} in the region $8\ \mathrm{K}^{-1} \geqslant 1000/T \geqslant 6\ \mathrm{K}^{-1}$ extrapolates at higher temperatures to the observed values of R_1, and must therefore represent a motional decrease of R_{2a}^{v} which occurs when the reciprocal of the correlation time

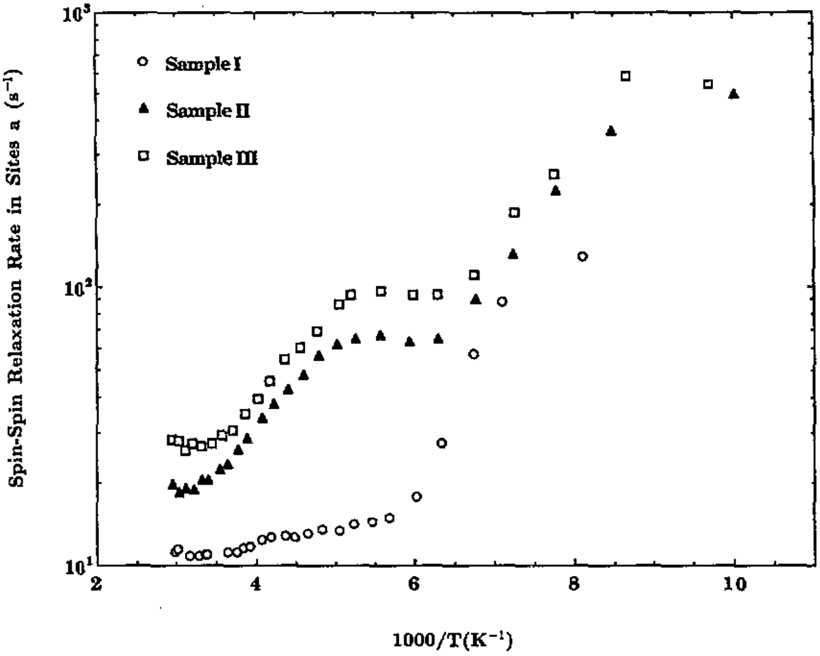

Figure 2. Measured relaxation rates of normal bulk deuterons, R_{2a}, as a function of inverse temperature in samples I, II and III. The temperature dependence reveals the coexistence of two relaxation processes.

becomes comparable with $R^{\mathrm{v}}_{2\mathrm{aRL}}$ (RL designates the rigid-lattice value of the variable). A consistent qualitative interpretation is thus obtained with $R^{\mathrm{v}}_{2\mathrm{a}}$ dominating at the lowest temperature; as T is raised its motional decrease allows $R^{\mathrm{d}}_{2\mathrm{a}}$ to take over. Thus, the flat central part of the curves represents $R^{\mathrm{d}}_{2\mathrm{aRL}}$, the rigid-lattice value of $R^{\mathrm{d}}_{2\mathrm{a}}$, which gives the magnitude of q^{d}_{zz}, the average long-range EFG produced by dislocations at the site of 'free' deuterons. The corresponding coupling constant expressed by $\nu^{\mathrm{d}}_{\mathrm{Q}} = e^2Qq^{\mathrm{d}}_{zz}/h \sim R^{\mathrm{d}}_{2\mathrm{aRL}}$ ranged between 13 Hz for the annealed sample and 94 Hz for the most deformed sample (table 1). It accounts for the overall rise of $R_{2\mathrm{a}}$ with cold-work since q^{d}_{zz} is increased by the larger density of dislocations. Motional decrease of the long-range

Table 1. Determination of dislocation densities from $R_{2\mathrm{a}}$ versus $1/T$ results.

Sample	T (K)	$R^{\mathrm{d}}_{2\mathrm{aRL}}$ (s^{-1})	$R^{\mathrm{d}}_{2\mathrm{a}}$ (s^{-1})	$\tau^{\mathrm{d}}_{\mathrm{a}}$ (10^{-2} s)	$\tau^{\mathrm{v}}_{\mathrm{a}}$ (10^{-8} s)	Λ ($10^{8}\ \mathrm{cm}^{-2}$)
I		12.8 ± 0.3				0.3
II	199.4	64.9 ± 1.3	61.7	9.4	5.4	7
	208.9	64.9 ± 1.3	56.8	4.0	3.1	9
III	197.9	94.3 ± 3.3	87.0	4.3	5.9	16
	209.5	94.3 ± 3.3	69.4	1.5	3.0	25

interaction R_{2a}^{d} follows at higher T. However, some caution is necesssary even when using the CPMG sequence because, as the deuterium diffusion coefficient increases, dephasing due to diffusion through background magnetic field gradients (Cotts 1978) and inhomogeneous EFGs can cause some decay of the CPMG signal, in addition to spin–spin relaxation, and consequently the *apparent* values of R_{2a} at the highest temperature ($1000/T \leqslant 3.5\ \mathrm{K}^{-1}$) in figure 2 are larger than the real spin–spin relaxation rate.

To analyse these data quantitatively, we use the relation of Kubo and Tomita (1954) which connects the motional correlation time with the relaxation rate and which incorporates the rigid-lattice value of spin–spin relaxation:

$$\tau_c = \tau_\infty\, e^{E_a/kT} = (4 \ln 2/\pi R_2) \tan[(\pi/2)(R_2/R_{2\mathrm{RL}})^2] = f(R_2). \qquad (1)$$

First, we deal with the vacancy-induced component R_{2a}^{v}. At the lowest T ($T \leqslant 230$ K for sample I and $T \leqslant 190$ K for samples II and III), we assume that R_{2a}^{d} takes its rigid-lattice value, and so $R_{2a}^{v} = R_{2a} - R_{2a\mathrm{RL}}^{d}$. Plotting $\ln f(R_{2a}^{v})$ versus $1/kT$ then yields a straight line of slope equal to the activation energy E_a^v and with y-intercept equal to $\ln \tau_{a\infty}^{v}$. In view of the fact that an obvious plateau has not been reached by the lowest-temperature points in figure 2, the procedure used was to make use of the well-established values of $(\tau_{a\infty}^{v})^{-1}$ and E_a^v ($3 \times 10^{12}\ \mathrm{s}^{-1}$ and 206 meV from Bogdan *et al* (1979) for example) to determine a value for $R_{2a\mathrm{RL}}^{v}$. The average result, which is 2.1 kHz, is consistent with the upper limit deduced earlier from measurements of R_1 by ourselves and others quoted in section 3.1. This somewhat smaller value of ν_Q^v reinforces the suspicion that measurements of R_1 are affected by a paramagnetic impurity contribution.

We now turn to the long-range component, R_{2a}^{d}, and discuss its value in terms of the dislocation density Λ in each sample. Observed relaxation rates R_{2a} smaller than $R_{2a\mathrm{RL}}^{d}$ are, to a good approximation, equal to R_{2a}^{d}. These are fitted to (1) to give the activation energy E_a^d and the correlation tine $\tau_{a\infty}^{d}$ associated with diffusion in the long-range fields. This activation energy should be similar to that for hopping between interstitial sites because the same deuteron motion is involved in both processes. However, the energies E_a^d derived in this way are about half the values of E_a^v. As already mentioned, we suspect that background magnetic field gradients are already corrupting R_{2a} results at temperatures much lower than ambient. Correspondingly, $\tau_{a\infty}^{d}$ would also be much smaller than the apparent value. Instead, τ_a^d may be deduced for samples II and III from the regions where motional decrease has just set in but where temperature is sufficiently low to preclude any data distortion by diffusion in inhomogeneous fields. Values are given in table 1.

A useful comparison of τ_a^v and τ_a^d at the same temperature gives an order of magnitude estimate of the dislocation density Λ in each sample. τ_a^v-values obtained from literature data are included in table 1. The mean distance travelled during a diffusional correlation time τ is proportional to $\sqrt{\tau}$; we assume to start with that this distance l for relaxation by dislocations is approximately given by half the mean distance between dislocations:

$$l = 1/\sqrt{\pi\Lambda}. \qquad (2)$$

The two correlation times τ_a^v and τ_a^d are thus related by:

$$\tau_a^d = 3(l/a)^2 \tau_a^v \qquad (3)$$

where $a = 2.84$ Å is the distance between nearest-neighbour octahedral sites. The factor three is included because relaxation by dislocations is effective only in a direction normal

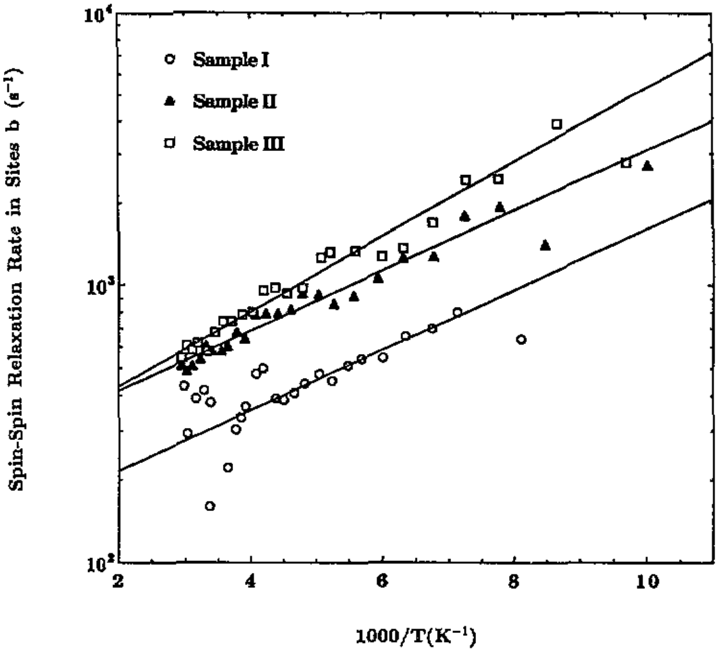

Figure 3. Measured relaxation rates of trapped deuterons, R_{2b}, as a function of inverse temperature in samples I, II and III. Fitted lines yield E_b and $\tau_{b\infty}$.

to the dislocation line. The relative dislocation densities may also be compared through the relation $R^{d}_{2aRL} \sim \nu^{d}_{Q} \propto \sqrt{\Lambda}$ (Kanert and Mehring 1971). As can be seen from table 1 this comparison is satisfactory for samples II and III and the relation may also be used to deduce the dislocation density in sample I. Λ-values are known to vary roughly between $10^8\ \mathrm{cm}^{-2}$ for annealed samples and $10^{12}\ \mathrm{cm}^{-2}$ for heavily deformed ones (see, e.g., Kirchheim 1981). In view of this, it appears that our values in table 1 are underestimated. This may be attributed to our choice of the distance over which the quadrupolar interaction due to dislocations changes appreciably. This distance would have to be reduced by a factor of approximately five in order to obtain Λ-values compatible with the literature. Such a reduction is not unreasonable.

3.2.2. Temperature dependence of R_{2b}: trapped deuterium. The faster spin–spin relaxation rate R_{2b} in all three samples is plotted as a function of inverse T in figure 3.

This rate, like R_{2a}, exhibits an increase with dislocation density which suggests that relaxation is also mainly quadrupolar in origin. The decrease of this rate with increasing T indicates a motional reduction of interactions caused by local EFGs at the sites of trapped deuterons. In this regime, where $R_{2b} \ll R_{2bRL}$, equation (1) takes the form:

$$\ln R_{2b} = E_b/kT + B \tag{4}$$

where $B = \ln(\tau_{b\infty} R^{2}_{2bRL}/2 \ln 2)$. Data points fitted to this equation yield activation energies E_b and correlation times at infinite temperature $\tau_{b\infty}$ associated with diffusion in the immediate vicinity of dislocations. Evaluation of $\tau_{b\infty}$ depends on a knowledge of R_{2bRL} which was not observed even at the lowest T. We therefore chose $R_{2bRL} = 10^4\ \mathrm{s}^{-1}$ (i.e. the quadrupolar coupling at the core of dislocations is of the order of 10 kHz) as an

Table 2. Results from R_{2b} versus $1/T$ data. $\tau_{b\infty}$ is calculated by assuming $R_{2bRL} = 10^4\ \mathrm{s}^{-1}$.

Sample	E_b (meV)	$\tau_{b\infty} R^2_{2bRL}$ (s^{-1})	$\tau^{-1}_{b\infty}$ (10^5 Hz)
I	22 ± 1	180 ± 10	5.5 ± 0.3
II	22 ± 1	351 ± 17	2.9 ± 0.2
III	27 ± 2	321 ± 20	3.1 ± 0.2

estimate to calculate $\tau^{-1}_{b\infty}$. This value is compatible with figure 3 and is not unreasonable as an average over the trapping region in comparison with the value of 50 kHz found by Lütgemier *et al* (1972) for ^{2}D in tetrahedral sites in BCC niobium where the distortion from local cubic symmetry amounts to 13%. In the present case the average distortion is certainly less than this. Results are given in table 2.

The dipolar contribution to R_{2bRL} is thought to be non-negligible. By using Van Vleck's second-moment calculations (Van Vleck 1948) and assuming that only octahedral sites are occupied (fully) in the vicinity of dislocations, we calculate $R^{\mathrm{dipolar}}_{2bRL} = 2.71 \times 10^3\ \mathrm{s}^{-1}$ which should essentially be independent of dislocation density.

The activation energy deduced for pipe diffusion of trapped particles ($E_b \simeq 0.024$ eV) is one order of magnitude smaller than that for 'free' deuterons which shows that it is easier, in principle, for particles to pipe diffuse along dislocations than to move in the perfect lattice in accordance with previous reports (Kirchheim 1981, Sicking *et al* 1983).

Correlation times at infinite temperature are 10^6–10^7 times longer than those in the 'normal' lattice which reflects the site-blocking effect of trapped deuterons through the blocking factor $1 - c_d$, where c_d is the concentration of particles in the vicinity of dislocations. The results (from $\tau^{-1}_{b\infty} = (1 - c_d) \times 3 \times 10^{12}\ \mathrm{s}^{-1}$) indicate that, while the average concentration in the sample means that about three quarters of the deuterium sites are filled, in core regions something approaching total occupation of sites occurs. This factor, being very close to zero in these sites, should make $\tau_{b\infty}$ very sensitive to the overall concentration of deuterium in the sample. We also note that this correlation time, although longer than the mean residence time in the 'normal' lattice at high temperatures, will become smaller than the latter at lower T owing to the different activation energies in the two sites. Motion becomes slower in the 'normal' lattice than in the deformed regions around dislocations below $T \simeq 200$ K.

Another effect that may be important results from the increase of trapping as temperature is lowered. Then, we would expect, on average, an increase of symmetry around a given deuteron that would result in a decrease of the local EFGs and consequently of the quadrupolar interaction. The local EFG would tend to the intrinsic value produced in the vicinity of a dislocation due only to the lattice distortion with all octahedral sites occupied. As a consequence, the observed activation energy may need to be corrected for this effect.

3.2.3. Temperature dependence of the fraction of trapped deuterons. The ratio of M_{b0}, the initial amplitude of component b in the CPMG sequence, to $M_{a0} + M_{b0}$, the total amplitude of the two components a and b, which represents the fraction ρ of deuterons in the trapping sites b was also recorded as a function of temperature for all samples. The results were somewhat inconclusive, however, since the value of ρ deduced depended somewhat on the spacing of the CPMG pulses. It was necessary to conduct the CPMG measurements with different time intervals $2t_p$ between the 180°-pulses in order to accommodate the 128 pulses in the magnetization decay times as it changed with cold-work and temperature. Although this adjustment of t_p did not affect the measured relaxation rates, it has revealed an apparent decrease of ρ with t_p which remains unexplained. This correlation might be connected with the effect, already mentioned, on the measurement of R_2 of diffusion in magnetic field gradients and, perhaps more importantly for ^{2}D, in inhomogeneous electric field gradients, both of which cause irreversible dephasing of the spins. Another effect which may be invoked to explain this $\rho(t_p)$ dependence is chemical exchange of deuterons between normal and trapping sites as discussed by Gil'manov and Fedotov (1970). On the time-scale of spin–spin relaxation, it is very likely that some deuterons will spend a non-negligible time at both sites resulting possibly in a distortion of the observed signal amplitudes of the two components.

Although inaccurate, our measured values for the fraction of trapped particles, which ranged between 0.11 for sample I and 0.57 for sample III, allow an estimation of the average trapping radius R_t around a dislocation line. Assuming that all trapping sites are occupied, R_t is then given by $(\rho c/\pi\Lambda)^{1/2}$, where c is the deuterium concentration in the sample. For the most deformed sample, a radius of $\simeq 30$ Å is obtained. In view of the dependence on t_p, these values of ρ and R_t should be taken to be indicative only.

In a simplified model, we can imagine the deuterons as being distributed between (only) two distinct energy levels whose separation is the trap binding energy E_T due to dislocations. The relative occupancy of these levels will depend on temperature following a Fermi–Dirac distribution (Han *et al* 1989) and the data for ρ as a function of cold-work and temperature should permit a determination of E_T and the ratio of 'normal' sites to trapping sites in each sample given a knowledge of the concentration of particles. However, because of the inaccuracy of ρ, it has not proved possible to obtain a value for E_T or for the ratio of 'normal' to trapping sites. E_T has however been estimated from previous observations to be 0.24 eV for ^{1}H (Schöneich *et al* 1985) and 0.187 eV for ^{3}T (Sicking *et al* 1983).

It is well known that dislocations may be of two types, edge and screw, or a mixture of both and it may be useful to question the similarity of the trap binding energies of these two types. Pure edge dislocations produce dilatational strains which we think trap hydrogen more effectively than shear strains generated by pure screw dislocations, and consequently we would expect a larger binding energy for the former type. A majority of dislocations, however, will have a mixed character and will be able to trap hydrogen to some extent resulting therefore in a distribution of trap binding energies between two limiting values. In a more realistic model therefore, more than two energy levels should be allowed for to describe the distribution of deuterons in the sample.

Despite this inconclusive measurement of ρ as a function of temperature and cold-work, it is nevertheless clear that the general trend of the fraction of trapped particles ρ is towards an increase with the dislocation density Λ. Almost all the points measured at approximately the same temperature with the same t_p exhibit an increase with Λ and an arithmetic average of ρ over the whole temperature range used for each of the three samples confirms the trend. These intensity observations thus support the hypothesis that the b component of the CPMG decay is due to deuterons trapped by dislocations.

4. Conclusions

This exploration of α'-phase palladium deuteride has led to a plausible depiction of the location and motion of deuterons, particularly in the presence of dislocations, as revealed by the temperature dependence of ^{2}D NMR spin–lattice and spin–spin relaxation rates.

In α'-PdD$_{\approx 0.6}$, the deuteron spin–spin relaxation is of mainly quadrupolar origin and indicates two sorts of environment in the lattice. The first one is constituted by normal octahedral interstitial sites which are slightly distorted by the long-range strain field of neighbouring dislocations. In addition, nuclei that are diffusing in these sites by hopping onto neighbouring vacancies experience a time-varying vacancy-induced quadrupolar coupling.

The second kind of environment in which some deuterons are accommodated is constituted by trapping sites in deformed regions in the immediate vicinity of dislocations, which are thought to be somewhat larger than the cores of dislocations as defined by elasticity theory. The long correlation time indicates near-complete occupation of these sites, effectively preventing the pipe diffusion found by others in samples with much lower concentration.

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