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Random walk theory of ^1H spin relaxation in TaV_2H_x

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Abstract

The theory of nuclear spin relaxation is developed for a random walk model of hydrogen diffusing between interstitial g sites in the cubic C15 AB_2 structure. The theory is applied in analysing the proton relaxation data for low H concentration in TaV_2H_x . The random walk theory results are used to assess the accuracy of a simpler modified Bloembergen–Purcell–Pound model. The temperature dependences of the two rates of jumps between g sites are deduced. The temperature dependence of the rate of jumps between g sites on a hexagon shows Arrhenius behaviour above ~ 50 K and a non-Arrhenius form at lower temperatures. The values of this jump rate are incompatible with the results from the analysis of quasielastic neutron scattering experiments. Possible reasons for this discrepancy are suggested.

1. Introduction

Hydrogen diffusion in intermetallic compounds is of interest in the development of hydrogen storage materials and the Laves-phase compounds AB_2 have attracted attention because many of these can absorb appreciable amounts of hydrogen [1]. Hydrogen occupies interstitial sites in the host metal structures and the hydrogen diffusion between these sites can be complicated in the Laves-phase compounds because there may be sets of inequivalent interstitial sites and multiple jump paths and jump rates. In addition, the hydrogen diffusion can show quantum behaviour at low temperatures and some ordered hydrogen configurations can occur [1]. Nuclear spin relaxation and quasielastic neutron scattering (QENS) are commonly used experimental techniques to study the site occupations and dynamics for hydrogen diffusion in metals [2, 3], but the analysis and interpretation of the experimental data is not a simple matter in the Laves-phase intermetallic compounds because of the above complications.

The most thoroughly studied example of the Laves-phase compounds is the cubic C15 Laves-phase compound TaV_2H_x in which hydrogen occupies a set of equivalent interstitial g sites that are arranged in linked hexagons [1]. There are two jump paths from a g site to nearest neighbours on a hexagon and one jump path to a near neighbour on an adjacent hexagon. Nuclear spin relaxation [4–6] and QENS [7, 8] studies in this system have shown the existence of two hydrogen jump rates corresponding to fast jumps Γ_1 within hexagons and slower

jumps Γ_2 between hexagons. It has also been established that there is a temperature-dependent fraction $1 - p$ of the hydrogen that do not participate in the Γ_1 and Γ_2 jumps. These ‘static’ hydrogen are postulated to be in ordered configurations.

Each of the nuclear spin relaxation and QENS methods needs a theoretical model of the hydrogen diffusion to interpret and analyse the experimental data. For low concentrations of hydrogen that diffuse between a set of equivalent interstitial sites in a metal, the simplest model is that a hydrogen atom will undergo an uncorrelated random walk with a jump rate Γ for hops between sites. This random walk model is called the Chudley–Elliott model when applied to QENS theory. It has been generalized to diffusion between sets of inequivalent interstitial sites which involves multiple jump rates [9] and to jumps between a localized set of sites [10]. The random walk model for diffusion between g sites in the C15 structure involves uncorrelated hops between sites with a jump rate Γ_1 for jumps within a hexagon and a jump rate Γ_2 for jumps between hexagons.

The application of the random walk model to calculating nuclear spin relaxation rates for diffusing protons in metals is more difficult. In this case the relaxation rates are linear combinations of spectral density functions that couple the diffusive motion of the hydrogen and the magnetic dipolar interactions between pairs of spins [2, 11]. A commonly used approximation that ignores the random walk details is the Bloembergen–Purcell–Pound (BPP) model [2]. The BPP model simply depends on the jump rate of a proton away from

a site and assumes the dipolar correlation function between a pair of spins becomes zero when a jump occurs. The BPP model has been used in some analyses of proton spin relaxation rates in TaV₂H_x [4, 5]. A modified BPP model was subsequently developed that describes the diffusion around a hexagon correctly but retains the BPP approximation for jumps between hexagons [12]. The random walk model includes the full details of the diffusive relative separation of a pair of relaxing spins and calculations based on this theory would enable a more rigorous analysis of the relaxation data and also allow the accuracy of the simpler models to be assessed. For proton–proton interactions (like-spin relaxation) there are additional complications due to correlations between the diffusion of each of a pair of protons, but for proton–metal interactions (unlike-spin relaxation) these correlations do not occur because the protons diffuse on a different set of sites to the metal nuclei. It is the latter case that is relevant to proton relaxation in TaV₂H_x.

The aim of the present work is to develop the random walk model for proton spin relaxation due to proton–metal nuclear interactions for hydrogen diffusion between the interstitial g sites in the cubic C15 AB₂ structure and apply this theory to analysing the proton relaxation data for TaV₂H_x. The emphasis in this work is on testing the consistency of the results obtained from analysing nuclear spin relaxation, QENS and diffusivity experimental data on the same system. The random walk theory results for the nuclear spin relaxation also enable an assessment of the accuracy of the simpler BPP models. The techniques and results obtained here will also be applicable to hydrogen in other Laves-phase intermetallic compounds.

Random walk theory of nuclear spin relaxation has previously been applied to hydrogen diffusion on Bravais lattices using a reciprocal space formalism [13]. This method has recently been extended to diffusion on interstitial sites in the cubic A15-type structure Nb₃AlH_x which form a non-Bravais lattice structure with multiple jump rates [14]. The reciprocal space method is, however, quite inefficient for the C15 structure because of the crystal structure and the large number (12) of g sites per unit cell. An alternative approach based on the Poisson distribution for the probability of n jumps of a diffusing atom in a time t is therefore developed in the following section.

2. Nuclear spin relaxation theory

Nuclear spin–lattice relaxation due to unlike-spin dipolar interactions will, in general, be characterized by a linear combination of two exponential decay rates [11]. In the case of protons diffusing in metal–hydrogen systems, it is usually the case that the metal nuclei relax much faster than the protons. The general equations [11] then show single exponential recoveries and the proton spin relaxation rate R_1 in polycrystalline samples is

$$R_1 = \frac{1}{15} \gamma_I^2 \gamma_S^2 \hbar^2 S(S+1) [J(\omega_I - \omega_S) + 3J(\omega_I) + 6J(\omega_I + \omega_S)] \quad (1)$$

where γ_I and γ_S are the gyromagnetic ratios for the proton and metal nucleus, respectively, S is the spin quantum number of

the metal nucleus, and $\omega_I = \gamma_I B$ and $\omega_S = \gamma_S B$, where B is the applied magnetic field. The spectral density function $J(\omega)$ is the Fourier transform

$$J(\omega) = 2 \operatorname{Re} \int_0^\infty G(t) e^{i\omega t} dt \quad (2)$$

of the correlation function $G(t)$ defined by

$$G(t) = \sum_{\alpha, \beta} \frac{P_2(\cos \theta_{\alpha\beta})}{r_\alpha^3 r_\beta^3} P(\mathbf{r}_\alpha, \mathbf{r}_\beta, t) \quad (3)$$

where $P(\mathbf{r}_\alpha, \mathbf{r}_\beta, t)$ is the probability of a proton and a metal nucleus being separated by \mathbf{r}_α at time zero and these same spins then being separated by \mathbf{r}_β at time t , $P_2(z)$ is a Legendre polynomial, and $\theta_{\alpha\beta}$ is the angle between \mathbf{r}_α and \mathbf{r}_β . Choosing a g site as origin, $G(t)$ can be written as

$$G(t) = \sum_{\alpha, \gamma} \frac{P_2(\cos \theta_{\alpha\beta})}{r_\alpha^3 r_\beta^3} P(\mathbf{r}_\gamma, t) \quad (4)$$

where \mathbf{r}_α are the metal sites, \mathbf{r}_γ are the g sites, $\mathbf{r}_\beta = \mathbf{r}_\alpha + \mathbf{r}_\gamma$, and $P(\mathbf{r}_\gamma, t)$ is the probability of a proton being displaced by \mathbf{r}_γ in a time t . At low hydrogen concentration, where each hydrogen follows an uncorrelated random walk, $P(\mathbf{r}_\gamma, t)$ can be written as

$$P(\mathbf{r}_\gamma, t) = \sum_{n=0}^\infty P_n(\mathbf{r}_\gamma) w_n(t) \quad (5)$$

where $P_n(\mathbf{r}_\gamma)$ is the probability of the hydrogen being displaced by \mathbf{r}_γ after n jumps, $w_n(t) = (\Gamma t)^n \exp(-\Gamma t)/n!$ is the Poisson distribution for the probability of n jumps of a particular hydrogen in a time t and $\Gamma = 2\Gamma_1 + \Gamma_2$ is the total jump rate away from a g site. The total number of jumps from each equivalent g site is determined by the total jump rate Γ , but the particular g site moved to at each jump will depend on the values of Γ_1 and Γ_2 . The spectral density function $J(\omega)$ can then be written as

$$J(\omega) = \sum_\gamma \sum_{n=0}^\infty S(\mathbf{r}_\gamma) P_n(\mathbf{r}_\gamma) w_n(\omega) \quad (6)$$

where $S(\mathbf{r}_\gamma)$ is a sum over the sites of the metal nuclei

$$S(\mathbf{r}_\gamma) = \sum_\alpha \frac{P_2(\cos \theta_{\alpha\beta})}{r_\alpha^3 r_\beta^3} \quad (7)$$

with $\mathbf{r}_\beta = \mathbf{r}_\alpha + \mathbf{r}_\gamma$, and where $w_n(\omega) = \operatorname{Re}[2\Gamma^n/(\Gamma - i\omega)^{n+1}]$ is the Fourier transform of $w_n(t)$. The expression (6) is a convenient form for computation of $J(\omega)$ because the $S(\mathbf{r}_\gamma)$ depend only on the crystal structure. These sums can be computed and stored for a suitable set of sites \mathbf{r}_γ . The probabilities $P_n(\mathbf{r}_\gamma)$ contain the dependence on the jump rates Γ_1 and Γ_2 and are the reason why the relaxation rate does not depend only on the total jump rate Γ as assumed in the BPP model. They can be generated numerically by enumerating all possibilities for a given n or by Monte Carlo simulations. In a simulation a jump from a g site will be to a neighbouring hexagon with probability Γ_2/Γ and will be to each of the

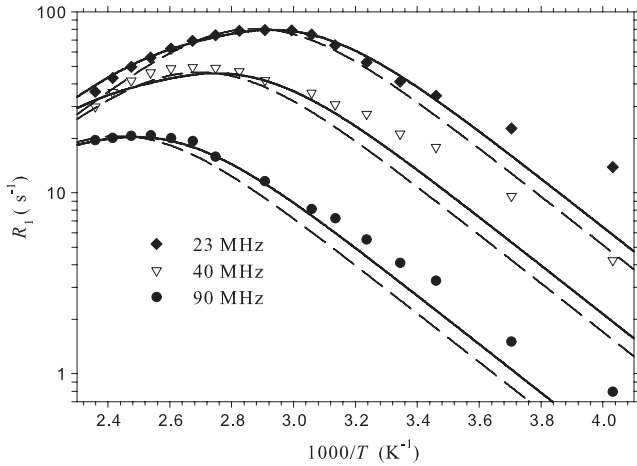


Figure 1. Temperature dependence of the dipolar part of the proton spin–lattice relaxation rate in TaV₂H_{0.1} at 23, 40 and 90 MHz (high temperature maximum). Symbols are experimental data [5]. The solid curves are a fit to the data using random walk theory. The dashed curves are a fit using the modified BPP model.

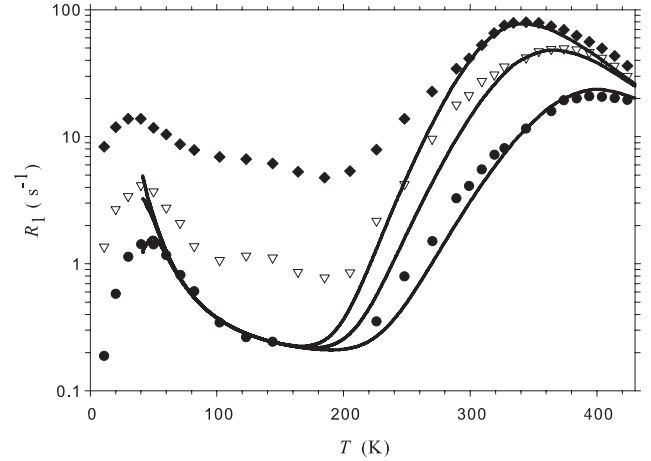


Figure 2. Temperature dependence of the dipolar part of the proton spin–lattice relaxation rate in TaV₂H_{0.1} at 23, 40 and 90 MHz. Symbols are experimental data [5]. The curves are the rates calculated from the modified BPP model as described in the text.

two nearest neighbours on a hexagon with probability Γ_1/Γ . The calculations of $P_n(\mathbf{r}_\gamma)$ in the following section used the enumeration method.

A useful modification of this procedure is that $S(\mathbf{r}_\gamma)P_n(\mathbf{r}_\gamma)$ in (6) can be replaced by $[S(\mathbf{r}_\gamma)P_n(\mathbf{r}_\gamma) - X]$ where X is a constant. This does not effect the value of $J(\omega)$ for non-zero ω but may improve the convergence rate of the summations. For example, if only Γ_1 jumps occurred, each hydrogen is confined to jumps on a single hexagon. The correlation function $G(t)$ then approaches a non-zero constant $\sum_{\gamma'} S(\mathbf{r}_{\gamma'})/6$ at large t , where the γ' sum is over the six localized sites. Choosing X as this constant improves the rate of convergence significantly. Such a procedure is useful for any circumstance where the hydrogen diffusion involves many localized jumps.

Another modification of the theory is useful when the localized jumps occur so rapidly that they effectively just average the dipolar interactions and the relaxation is caused by the slower jump rate. Under these circumstances the Poisson distribution $w_n(t)$ can refer to the number n of the slower jumps in a time t , and the $P_n(\mathbf{r}_\gamma)$ refers to the probability of the proton being at \mathbf{r}_γ after n steps, where a step consists of an averaging over the localized sites followed by a jump away from these sites.

The above numerical methods can calculate the spectral density function $J(\omega)$ using random walk theory for general values of the jump rates Γ_1 and Γ_2 . The results from these calculations can be used to assess the accuracy of approximate analytic spectral density functions. The BPP model corresponds to only retaining the term $n = 0$ in equations (5) and (6) and only depends on the total jump rate away from a site. This is equivalent to the dipolar correlation function being reduced to zero when the first jump occurs. The modified BPP model [12] involves a rigorous random walk analysis of the Γ_1 jumps around a hexagon together with the approximation that a Γ_2 jump to a neighbouring hexagon that reduces the correlation function to zero as for the BPP model. The spectral density functions for this model are given in [12].

A special case of this modified BPP model is when $\Gamma_1 \rightarrow \infty$. This corresponds to a BPP model for the case in the preceding paragraph ($n = 0$). A similar model could be used for the case of rapid jumps Γ_2 between hexagons and slower jumps Γ_1 within hexagons.

3. Application to TaV₂H_x

The proton spin–lattice relaxation rate R_1 in TaV₂H_x has been measured as a function of temperature and resonance frequency for a range of values of x [5] but only the low H concentration case $x = 0.1$ will be considered here. Two maxima in R_1 as a function of temperature occur for each resonance frequency. The data in the vicinity of the high temperature maximum is shown in figure 1 as a function of $1000/T$, and the data over the full temperature range is shown as a function of T in figure 2. The contribution to the relaxation from the conduction electrons has been subtracted [5]. The magnetic dipolar contribution to the relaxation is dominated by interactions between protons and metal nuclei and can be calculated from equation (1). Contributions from both the Ta and V nuclei have been included in all calculations.

Since $\Gamma_1 \gg \Gamma_2$ the relaxation at high temperatures is a consequence of the slower Γ_2 jumps between hexagons with many rapid jumps of hydrogen around a hexagon occurring between each jump between hexagons. The relaxation can therefore be calculated from random walk theory with the Poisson distribution referring to the number of Γ_2 jumps. The high temperature form of Γ_2 can be deduced from the measured value of the diffusivity D [15], which is of Arrhenius form. For $\Gamma_1 \gg \Gamma_2$, the jump rate Γ_2 is related to the diffusivity by $\Gamma_2 = 48D/a^2$ [12] where a is the lattice parameter. The result for Γ_2 is an activation energy $E_2 = 0.267$ eV and a prefactor $\Gamma_{20} = 2.57 \times 10^{12} \text{ s}^{-1}$. A fit to the data in figure 1 was made using these parameters with the addition of a multiplicative scaling factor p in the relaxation rate to account for the fraction of mobile hydrogen that contribute to the relaxation, and a

factor A to scale the magnitude of Γ_{20} . The value of $p = 0.78$ was chosen to fit the values of the relaxation maxima and the value of $A = 0.58$ was chosen to fit the temperatures at which the maxima occur. The calculations included up to seven jumps between hexagons. Also shown in figure 1 is a fit using zero jumps between hexagons which corresponds to the modified BPP model [12]. In this case $p = 0.70$ and $A = 0.47$.

It can be seen that the random walk model provides an excellent fit to the high temperature experimental data with only a small adjustment $A = 0.58$ to the frequency Γ_{20} from the diffusivity. A fit could also have been made by including a small adjustment to the activation energy rather than the prefactor. The modified BPP model also provides a reasonable fit to the data, but produces narrower maxima than the random walk theory. Both models underestimate the relaxation rates at lower temperatures. The fraction p of mobile hydrogen will decrease as the temperature decreases and this effect would reduce the calculated relaxation rates further on the low temperature side of the maximum. The temperature dependence of p cannot therefore account for the underestimation of the relaxation rates at lower temperatures.

The relaxation data over the whole temperature range is shown in figure 2 as a function of temperature. The magnitude of the low temperature maxima are much smaller than the high temperature maxima. The values of the high temperature maxima are consistent with the $1/\omega$ dependence expected from equation (1) for dipolar relaxation. But, as noted by Buzlukov and Skripov [5], this is not the case for the low temperature maxima, which suggests an additional relaxation mechanism that increases with decreasing frequency. The postulated additional mechanism was cross-relaxation between the proton and Ta quadrupolar nuclear spins [2, 16] which could be relevant at low temperatures and it was suggested that this relaxation contribution would be negligible for the higher frequency 90 MHz data [5]. An alternative explanation of the anomalous behaviour of the low temperature data that the dipolar relaxation has a distribution of jump rates was rejected because it would require an unreasonably broad distribution of rates [5]. The assumption that the 90 MHz data is due to unlike-spin dipolar relaxation and that the lower frequency data involves relaxation contributions from another process will also be made here. Only the 90 MHz data will therefore be analysed in terms of the random walk model.

In the vicinity of the low temperature maximum the dipolar relaxation is due to the faster jump rate Γ_1 within a hexagon. The slower jump rate Γ_2 is too slow to have any influence on the relaxation at low temperatures. The relaxation rate in this region can be calculated from the simpler modified BPP model since this is identical to the random walk model when $\Gamma_2 = 0$. The temperature dependence $p(T)$ of the fraction of mobile hydrogen must also be taken into account and this was estimated as follows. The value of p at the temperature at which the low temperature maximum occurs can be estimated from the ratio of the observed maximum rate to the calculated rate from equation (1) and is $p = 0.050$ at $T = 45$ K. The function $p(T)$ was then assumed to be linear between the values of p deduced from the high and low temperature maxima. This procedure neglects the effect

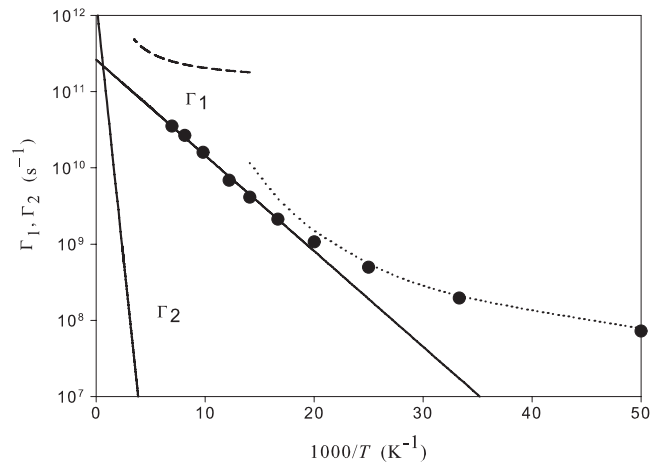


Figure 3. Temperature dependence of the jump rates Γ_1 and Γ_2 . The circles are the values of Γ_1 obtained from the fit to the low temperature relaxation data points. The solid line for Γ_1 is the Arrhenius fit to the high temperature part of this data, and the dotted line is the $\Gamma_1 = \Gamma_{10} \exp(T/T_0)$ fit to the low temperature part of this data. The Γ_1 deduced from the QENS data [6] is the dashed line. The solid line for Γ_2 is the Arrhenius form obtained from the diffusion data and fit to the high temperature relaxation data.

that the observed relaxation maximum will occur at a lower temperature than the calculated maximum when the decreasing form of $p(T)$ with temperature is taken into account. The calculated relaxation rates were then used to determine the value of Γ_1 at the temperature of each low temperature experimental relaxation data point. The values of Γ_1 obtained are shown in figure 3. The data show approximate Arrhenius behaviour for high temperatures. An Arrhenius fit gives an activation energy of 0.025 eV and a prefactor of $2.6 \times 10^{11} \text{ s}^{-1}$. The enhancement of Γ_1 from Arrhenius form at low temperatures is characteristic of quantum diffusion [5, 17] and suggests that the hydrogen jumps on a hexagon exhibit quantum diffusion below ~ 50 K. The Arrhenius form of Γ_2 from the fit to the high temperature region is also shown in figure 3.

The temperature dependence of p and Γ_1 have also been obtained from QENS data for TaV_2H_x with $x = 0.65$ in the temperature range 70–290 K [8]. These QENS results for the temperature dependence of p are reasonably consistent with the values deduced here from the relaxation theory, but this is not the case for Γ_1 . In the QENS analysis the temperature dependence of Γ_1 was fitted to the function $\Gamma_{10} \exp(T/T_0)$ with $\Gamma_{10} = 1.30 \times 10^{11} \text{ s}^{-1}$ and $T_0 = 220$ K. This result for Γ_1 is shown as the dashed line in figure 3. The dotted line in figure 3 shows the fitting of this function to the low-temperature Γ_1 data from the proton relaxation data, with parameters $\Gamma_{10} = 1.1 \times 10^7 \text{ s}^{-1}$ and $T_0 = 10.2$ K which are very different from the QENS fit parameters. It can be seen that there is a significant difference in both the magnitude and functional forms of Γ_1 obtained from the relaxation data and from the QENS data. The hydrogen concentration $x = 0.65$ in the QENS study [8] is higher than the $x = 0.1$ in the spin relaxation data [5], but the jump rate increases with decreasing hydrogen concentration [5] and so adjusting the QENS jump

rate for a lower x would increase the discrepancy. Further, calculating the relaxation rate from equation (1) using the QENS results for p and Γ_1 gives a relaxation rate too small to be observable. The values of the jump rate Γ_1 deduced from the QENS analysis and from the spin relaxation analysis are therefore incompatible.

The above analyses of the relaxation data has considered the high- and low temperature data independently. The modified BPP model provides an approximate analytic spectral density function that can be used over the complete temperature range. The results obtained by using this function with the forms of p , Γ_1 and Γ_2 deduced above from the relaxation data are shown in figure 2 as a function of temperature. The results at low temperatures are the same as those from the random walk theory, the results at high temperatures are similar to those in figure 1, and the results in the region between the maxima give a reasonable fit to the 90 MHz data. The modified BPP model therefore provides a useful and simple approach for analysing the relaxation data over the entire temperature range, subject to the effect that it produces maxima that are somewhat too narrow at high temperatures.

4. Discussion and conclusions

Using random walk theory has enabled an accurate calculation of proton relaxation rates for low concentrations of hydrogen diffusing between interstitial g sites in the cubic C15 AB₂ structure. The application of the theory to proton relaxation in TaV₂H_x has shown that the temperature-dependent jump rate Γ_2 between hexagons deduced from diffusivity measurements [15] is consistent with the high temperature relaxation data.

The temperature dependence of the jump rate Γ_1 between g sites on a hexagon was obtained from the low temperature relaxation data. This jump rate is of Arrhenius form above ~ 50 K and showed non-Arrhenius form that is evidence of quantum diffusion at lower temperatures. These values of Γ_1 are incompatible with the values deduced from QENS experiments [8]. A possible reason for this discrepancy could be that the model of only considering Γ_1 jumps that was used in analysing the QENS data [8] is insufficient. Another possibility is that the low temperature relaxation maximum for a frequency of 90 MHz also has a contribution from cross-relaxation as has been argued for the 23 and 40 MHz data [5]. A further possibility is that the hydrogen jumps at low temperatures are more complicated than just the Γ_1 and Γ_2 jumps of isolated hydrogen; jumps from ordered configurations of hydrogen could become significant at low temperatures in either, or both, of the spin relaxation and

QENS data. This could be the case even at low hydrogen concentrations if the ordered configurations were clusters due to short range hydrogen–hydrogen interactions. In addition, recent measurements of proton spin relaxation in nanostructured TaV₂H_x have shown that the relaxation maxima at low temperatures disappear as the grain size of the material is reduced [6]. This has been attributed [6] to the jump rates Γ_1 within hexagons being sensitive to slight distortions in the hexagons.

The high temperature diffusive behaviour of hydrogen in TaV₂H_x appears to be well understood but the low temperature behaviour shows anomalies between the interpretations of the nuclear spin relaxation data and QENS data for similar diffusion models. Further theoretical and experimental effort would be useful in clarifying the low temperature diffusive behaviour of hydrogen in TaV₂ and other Laves-phase intermetallic compounds. The random walk theory of nuclear spin relaxation developed here for diffusion between interstitial g sites in the cubic C15 structure should also be applicable to other structures. It can provide a rigorous calculation of the relaxation rates at low hydrogen concentrations and provide an assessment of the accuracy of simpler models such as the BPP and modified BPP model for TaV₂H_x [12].

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