

A modified Bloembergen–Purcell–Pound model for nuclear spin relaxation of hydrogen in the C15 AB₂ structure: TaV₂H_x and ZrCr₂H_x

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2005 J. Phys.: Condens. Matter 17 7561

(<http://iopscience.iop.org/0953-8984/17/48/009>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 129.252.86.83

The article was downloaded on 28/05/2010 at 06:53

Please note that [terms and conditions apply](#).

A modified Bloembergen–Purcell–Pound model for nuclear spin relaxation of hydrogen in the C15 AB₂ structure: TaV₂H_x and ZrCr₂H_x

C A Sholl

Physics and Electronics, University of New England, Armidale, NSW 2351, Australia

E-mail: csholl@metz.une.edu.au

Received 26 August 2005, in final form 17 October 2005

Published 11 November 2005

Online at stacks.iop.org/JPhysCM/17/7561

Abstract

The BPP model for nuclear spin relaxation is modified to account rigorously for jumps of hydrogen within g site hexagons in the C15 AB₂ structure. The theory is applied to proton relaxation data for low H concentrations in TaV₂H_x and ZrCr₂H_x. It is shown that the data are consistent with the results of quantum diffusion calculations, diffusivity measurements and H–H interaction effects deduced from quasielastic neutron scattering experiments.

1. Introduction

The diffusion of hydrogen in intermetallic compounds with the cubic C15 AB₂ structure has been studied by pulsed-field-gradient nuclear magnetic resonance (PFG-NMR), nuclear spin relaxation, quasielastic neutron scattering (QENS), and anelastic relaxation (see, for example, Skripov 2004). This range of experimental techniques is valuable in understanding the behaviour of the H diffusion in such complicated structures where there are inequivalent interstitial sites occupied by the H, there are multiple H jump rates, there is good evidence for quantum diffusion, and partial ordering of H can occur. There have also been recent advances in theoretical calculations of diffusion of H in these structures (Bhatia *et al* 2004, Bhatia and Sholl 2005) and in the theory connecting the H jump rates and the diffusivity D (Sholl 2005).

The technique of nuclear spin relaxation is especially useful because it can be used to study diffusion over a wide temperature range, results can be obtained at different resonant frequencies, and in some cases the relaxation of metal nuclei and D can be measured in addition to the H relaxation rates. The proton nuclear spin relaxation rates are linear combinations of spectral density functions of the magnetic dipolar interactions between pairs of spins undergoing relative diffusion. An approximation often used for the spectral density functions is the Bloembergen–Purcell–Pound (BPP) model (Bloembergen *et al* 1948). The BPP model leads to a Lorentzian spectral density function which has the virtues of simplicity and ease of use. It is also often reasonably accurate for nuclear spin relaxation due to three-dimensional diffusion in cubic crystals (Sholl 1993).

The BPP approximation is not, however, a good approximation for describing localized jumps which do not lead to long range diffusion. An example is H in hexagonal α -ScH_x (Lichty *et al* 1988). In this case the H form pairs separated by a metal atom at low temperatures and the H undergo fast localized jumps between a pair of interstitial sites, together with a slower jump rate away from the pair of sites. The spectral density functions in this case were calculated by a rigorous model of jumping between the pair of sites and by combining this with the BPP model for the slower jumps away from the pair of sites.

The H occupy interstitial g and e sites in the C15 intermetallic compounds (Skripov 2004). The g sites form linked hexagons where the g–g distance is different for intra-hexagon jumps to that for inter-hexagon jumps. Rapid jumps within a hexagon will therefore not lead to long range diffusion and the BPP model could be inadequate in this case. An aim of this paper is to develop a more accurate theory for the spectral density functions for this system. The theory is described in the following section.

In section 3, the theory is applied to two examples where it is known that the H occupies mainly g sites. One example is TaV₂H_x for which the proton relaxation shows two well separated maxima at different temperatures. The high temperature maximum has been identified as being associated with the jumps between hexagons and the low temperature maximum associated with jumps within hexagons (Skripov 2004). The other example is ZrCr₂H_x for which only a single asymmetric maximum is observed in the proton relaxation rate. In both of these examples there are also H diffusivity data available, together with some other information about H location and jump rates from QENS and theoretical calculations. The aim of applying the present relaxation theory to these systems is not to find the best fit to the relaxation data by varying a set of adjustable parameters. Rather, the aim is to assess the accuracy of the relaxation theory by examining its consistency with data from these other sources wherever this is possible.

2. Nuclear spin relaxation and spectral density functions

In general, H can occupy both e and g sites in C15 AB₂H_x compounds. An e site has three neighbouring g sites which are each on different hexagons. A g site has one neighbouring e site, two neighbouring g sites on a hexagon and one neighbouring g site on an adjacent hexagon (Eberle *et al* 2002). The jump rates between the sites are defined as Γ_{ge} from a g site to an e site, Γ_{eg} from an e site to a g site, Γ_1 for jumps between g sites on a hexagon, and Γ_2 for jumps between g sites on adjacent hexagons. Direct jumps between e sites are not considered. The probabilities c_e and c_g of H at e and g sites, respectively, for the C15 structure AB₂H_x are related to the jump rates by the principle of detailed balance (Bhatia *et al* 2004).

The first relaxation case to be considered is unlike spin relaxation of H due to magnetic dipolar interactions with fixed metal spins. The nuclear spin–lattice relaxation rate R_{1U} of diffusing spins I (protons) interacting with fixed S (metal) spins is (Abragam 1961, Bhatia *et al* 2004)

$$R_{1U} = \frac{1}{15} \gamma_I^2 \gamma_S^2 \hbar^2 S(S+1) \left\{ \frac{4c_e}{x} [J_e(\omega_I - \omega_S) + 3J_e(\omega_I) + 6J_e(\omega_I + \omega_S)] + \frac{12c_g}{x} [J_g(\omega_I - \omega_S) + 3J_g(\omega_I) + 6J_g(\omega_I + \omega_S)] \right\} \quad (1)$$

where I and S are the spin quantum numbers, γ_I and γ_S are the spin gyromagnetic ratios, ω_I and ω_S are the resonant frequencies of the spins and $J_e(\omega)$ and $J_g(\omega)$ are spherically averaged spectral density functions.

The spectral density functions may be written in the form

$$J(\omega) = \sum_{\alpha,\beta} \frac{P_2(\cos \theta_{\alpha\beta})}{r_\alpha^3 r_\beta^3} P(\mathbf{r}_\alpha, \mathbf{r}_\beta, \omega) \quad (2)$$

where $P_2(z) = (3z^2 - 1)/2$, $\theta_{\alpha\beta}$ is the angle between \mathbf{r}_α and \mathbf{r}_β , and $P(\mathbf{r}_\alpha, \mathbf{r}_\beta, \omega)$ is the Fourier transform

$$P(\mathbf{r}_\alpha, \mathbf{r}_\beta, \omega) = 2 \operatorname{Re} \int_0^\infty P(\mathbf{r}_\alpha, \mathbf{r}_\beta, t) e^{i\omega t} dt. \quad (3)$$

$P(\mathbf{r}_\alpha, \mathbf{r}_\beta, t)$ is the probability that a pair of spins will be separated by \mathbf{r}_β at time t if the relative separation of the pair of spins was \mathbf{r}_α at time zero. The origin of the vectors \mathbf{r}_α is an e site for $J_e(\omega)$ and is a g site for $J_g(\omega)$, with the α sums taken over the sites of the metal spins.

The BPP approximation assumes $P(\mathbf{r}_\alpha, \mathbf{r}_\beta, t) = \delta_{\alpha,\beta} e^{-\Gamma t}$ where Γ is the jump rate of H away from a site and $e^{-\Gamma t}$ is the probability of no jump in a time t . It assumes that the correlation between the spins is destroyed when a jump occurs. The spectral density function is then

$$J_{\text{BPP}}(\omega) = 2S_1 \frac{\Gamma}{\Gamma^2 + \omega^2} \quad (4)$$

where $S_1 = \sum_\alpha r_\alpha^{-6}$. This approximation will be assumed for $J_e(\omega)$ with $\Gamma = \Gamma_e = 3\Gamma_{\text{eg}}$, where Γ_e is the jump rate away from an e site. The sum S_1 includes all metal atom sites relative to an e site.

The BPP approximation ignores the effect on the magnetic dipolar correlation function of a diffusing spin remaining in the vicinity of its starting point after a jump has occurred. This approximation is reasonable if the spin diffuses away from the site rapidly, but could be a poor approximation for cases such as rapid diffusion around a hexagon before a jump occurs to another hexagon or an e site. This effect could be especially significant for $J_g(\omega)$. The effect of diffusion around hexagons can be included by treating the jumps around a hexagon exactly and using the BPP approximation for the jumps to a different hexagon and for jumps to an e site.

Consider a spin at a g site that has a jump rate Γ_1 to a neighbouring site on a hexagon, and a jump rate Γ_2 to a neighbouring site on an adjacent hexagon. The total jump rate away from a site is $\Gamma_g = 2\Gamma_1 + \Gamma_2 + \Gamma_{\text{ge}}$. It is assumed that there cannot be more than one spin on each hexagon and site blocking effects on jumps are neglected because only low H spin concentrations will be considered. Labelling the sites cyclically on the hexagon $i = 1$ to 6, and assuming the spin is at site $i = 1$ at time zero, the probability $P_i(t)$ of the spin being at site i at time t is given by the equations

$$\frac{dP_1}{dt} = -\Gamma_g P_1 + 2\Gamma_1 P_2 \quad (5)$$

$$\frac{dP_2}{dt} = -\Gamma_g P_2 + \Gamma_1 (P_1 + P_3) \quad (6)$$

$$\frac{dP_3}{dt} = -\Gamma_g P_3 + \Gamma_1 (P_2 + P_4) \quad (7)$$

$$\frac{dP_4}{dt} = -\Gamma_g P_4 + 2\Gamma_1 P_3 \quad (8)$$

and where $P_2 = P_6$ and $P_3 = P_5$ by symmetry. Taking the Fourier transform (3) of these equations and using the initial condition $P_i(0) = \delta_{i1}$, the solutions for $P_i(\omega)$ may be written

as

$$P_1(\omega) = \frac{2z(z^2 - 3\Gamma_1^2)}{z^2(z^2 - 3\Gamma_1^2) - 2\Gamma_1^2(z^2 - 2\Gamma_1^2)} \quad (9)$$

$$P_2(\omega) = P_6(\omega) = \frac{\Gamma_1(z^2 - 2\Gamma_1^2)}{z(z^2 - 3\Gamma_1^2)} P_1(\omega) \quad (10)$$

$$P_3(\omega) = P_5(\omega) = \frac{z\Gamma_1}{z^2 - 2\Gamma_1^2} P_2(\omega) \quad (11)$$

$$P_4(\omega) = \frac{2\Gamma_1}{z} P_3(\omega) \quad (12)$$

where $z = \Gamma_g - i\omega$.

Using equation (2) the spectral density function $J_g(\omega)$ then becomes

$$J_g(\omega) = \text{Re} \sum_{i=1}^4 S_i P_i(\omega) \quad (13)$$

where $S_i = \sum_{\alpha,\beta(i)} P_2(\cos\theta_{\alpha\beta})/(r_\alpha r_\beta)^3$. The vectors \mathbf{r}_β in these sums are $\mathbf{r}_\beta = \mathbf{r}_\alpha$ for $i = 1$, \mathbf{r}_β includes the two nearest neighbour sites of \mathbf{r}_α on a hexagon for $i = 2$, \mathbf{r}_β includes the two second nearest neighbour sites of \mathbf{r}_α on a hexagon for $i = 3$, and \mathbf{r}_β is the single third nearest neighbour site of \mathbf{r}_α on a hexagon for $i = 4$.

A special case of this theory that is of interest is when $\Gamma_{ge} = 0$ and $\Gamma_1 \gg \Gamma_2$, corresponding to much faster jumps within a hexagon than for jumps between hexagons. In this case the theory gives two well separated maxima in the relaxation rates at high and low temperatures as for the experimental data for TaV₂H_x (Skripov 2004). This can be seen as follows. In the limit $\Gamma_1 \rightarrow \infty$ all of the $P_i(\omega)$ in equations (9)–(12) become identical and $J_g(\omega)$ becomes

$$J_{\text{high}}(\omega) = \frac{\sum_{i=1}^4 S_i}{3} \frac{\Gamma_2}{\Gamma_2^2 + \omega^2}. \quad (14)$$

This is of the BPP form in equation (3), but with a different proportionality factor. The consequent relaxation rates depend only on the slower jump rate Γ_2 and are relevant to the relaxation in the vicinity of the high temperature maximum in TaV₂H_x.

The limit $\Gamma_2 \rightarrow 0$ gives $J_{\text{low}}(\omega)$ which depends only on the faster jump rate Γ_1 and is not of BPP form. These spectral density functions give the form of the low temperature maximum in the relaxation rates. The functions $\omega P_i(\omega)$ as a function of ω/Γ_1 are shown in this limit in figure 1. The spectral density function in this limit depends on the crystal structure through the summations S_i in equation (13). An example of a comparison between $\omega J_{\text{low}}(\omega)$ and the BPP result is shown in figure 2 for the values of S_i for H–V interactions given in table 1. The BPP result is also shown shifted to fit the position and magnitude of the maximum of $\omega J_{\text{low}}(\omega)$ to enable a comparison of the shapes of the maxima. It can be seen that the BPP peak is narrower, is larger and has its maximum at different ω/Γ_1 to the function describing diffusion on a localized hexagon. The asymptotic slopes of the BPP curves are the same as $\omega J_{\text{low}}(\omega)$ in both the low and high ω/Γ_1 limits.

The above theory of the spectral density functions can also be adapted to the case of like spin relaxation of H due to magnetic dipolar interactions between pairs of diffusing H. The relaxation rate R_{1L} of the H is then (Abragam 1961, Bhatia *et al* 2004)

$$R_{1L} = \frac{1}{5} \gamma_I^4 \hbar^2 I(I+1) \left\{ \frac{4c_e}{x} [J_{eg}(\omega_I) + 4J_{eg}(2\omega_I)] \right. \\ \left. \frac{12c_g}{x} [J_{gg}(\omega_I) + 4J_{gg}(2\omega_I) + J_{ge}(\omega_I) + 4J_{ge}(2\omega_I)] \right\} \quad (15)$$

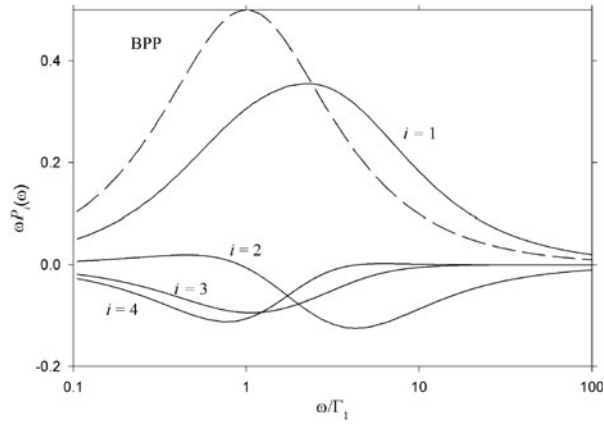


Figure 1. The real part of the functions $\omega P_i(\omega)$ as a function of ω/Γ_1 in the limit $\Gamma_2 \rightarrow 0$, and the corresponding BPP function.

Table 1. Values of the lattice sums S_i in units of a^{-6} . The sums for e-g interactions are three times the values for g-e interactions.

	S_1	S_2	S_3	S_4
TaV ₂ H _x g-Ta	7.57×10^3	9.39×10^3	527	-835
TaV ₂ H _x g-V	1.11×10^4	1.27×10^4	6.44×10^3	3.02×10^3
ZrCr ₂ H _x No restriction				
g-g	2.07×10^5	1.79×10^5	157	-3.27×10^4
g-e	9.42×10^4	8.17×10^4	8.81×10^3	2.06×10^3
ZrCr ₂ H _x $r_{\min} = 2.1 \text{ \AA}$				
g-g	1.19×10^4	3.10×10^4	1.95×10^4	7.84×10^3
g-e	4.05×10^3	9.86×10^3	6.06×10^3	2.40×10^3
ZrCr ₂ H _x $r_{\min} = 2.0 \text{ \AA}$				
g-g	1.66×10^4	3.86×10^4	1.83×10^4	7.84×10^3
g-e	5.83×10^3	1.46×10^4	7.97×10^3	3.16×10^3

where the spectral density functions are the following. $J_{gg}(\omega)$ is for the case of both spins initially on g sites. It is of the same form as $J_g(\omega)$ but has each of the jump rates in it doubled to account for either of the pair of spins undergoing jumps, the sums S_i are for interactions between pairs of g sites and a multiplicative factor of c_g is included to account for the probability of a spin at site \mathbf{r}_α . $J_{eg}(\omega)$ is for the case of one spin at an e site at the origin and the other spin at a g site with probability c_g . It is also of the form of $J_g(\omega)$ but with Γ_g replaced by $\Gamma_g + \Gamma_{eg}$, the sums S_i are for interactions between e and g sites and a multiplicative factor of c_g is included. The spectral density function $J_{ge}(\omega)$ has e and g interchanged in $J_{eg}(\omega)$.

The above theory has neglected site-blocking effects on H jumps so is valid at low H concentrations. The unlike spin relaxation theory is applied to TaV₂H_x and the like spin relaxation theory is applied to ZrCr₂H_x in the following sections.

3. Nuclear spin relaxation in TaV₂H_x

The proton relaxation rate in TaV₂H_x has been measured as a function of temperature for a range of H concentration x and frequency (Buzlukov and Skripov 2004). Only the low concentration

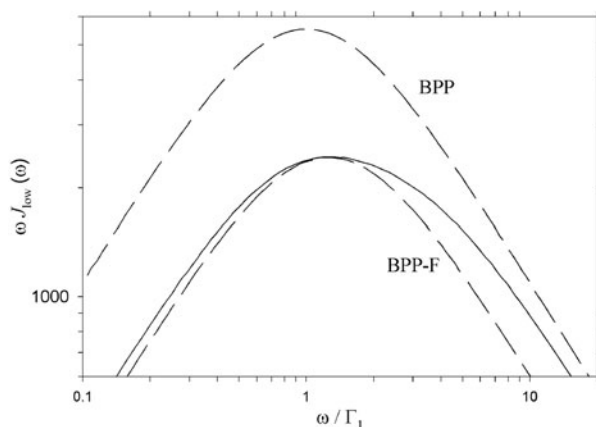


Figure 2. The function $\omega J_{\text{low}}(\omega)$ as a function of ω/Γ_1 in the limit $\Gamma_2 \rightarrow 0$ for the values of S_i for H–V interactions (solid curve). The corresponding BPP function is shown as the dashed curve, together with this curve translated to fit the position and magnitude of the maximum of the solid curve (BPP-F).

data for $x = 0.10$ will be considered here since interaction and correlation effects should be less at low concentrations. The proton relaxation data as a function of temperature show a high temperature maximum at 400 K and another smaller maximum at 40 K for each resonance frequency (23, 40 and 90 MHz). The low temperature maxima have been attributed to rapid jumps Γ_1 between g sites within hexagons and the high temperature maxima attributed to slower Γ_2 jumps between g sites between adjacent hexagons.

The relaxation of protons in TaV_2H_x is dominated by the dipolar interactions between metal nuclei and protons, rather than the interactions between pairs of H. The relaxation rate is therefore given by equation (1). Interactions of H with both the Ta nuclei and the V nuclei have been included in the calculations. The values of lattice sums S_i for g sites are given in the table in the following section, taking the positional parameters for the g sites to be $X = 0.055$ and $Z = 0.888$ (Fischer *et al* 1997). The lattice parameter is 7.166 \AA (Buzlukov and Skripov 2004). It is assumed that only the g sites are occupied by H.

Since the relaxation maxima are well separated, the high temperature data can be analysed using the spectral density function $J_{\text{high}}(\omega)$ given by equation (14). If $\Gamma_1 \gg \Gamma_2$ the values of Γ_2 in the high temperature region can be deduced from the proton diffusivity D measured by PFG-NMR in $\text{TaV}_2\text{H}_{1.24}$ (Majer *et al* 1995) between 334 and 484 K. The diffusivity shows approximate Arrhenius form with a prefactor of $27.5 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ and an activation energy of 0.267 eV in this temperature range. In the low concentration limit the diffusivity is related to the jump rates by Sholl (2005)

$$D = \frac{a^2}{48} \frac{1}{\Gamma_1^{-1} + \Gamma_2^{-1}} \quad (16)$$

so that $\Gamma_2 = 48D/a^2$ if $\Gamma_1 \gg \Gamma_2$ and neglecting a small correlation effect for D at $x = 1.24$. These values of Γ_2 and $J_{\text{high}}(\omega)$ were used to calculate the high temperature relaxation rates with two adjustable parameters. A multiplicative parameter p was used to fit the value of the maximum, and the jump rate Γ_2 was scaled by a factor A to fit the temperature at which the maximum occurs for the 23 MHz data.

The results of the fit to the experimental data (Buzlukov and Skripov 2004), after subtracting the electronic contribution to the relaxation rate, are shown in figure 3. The

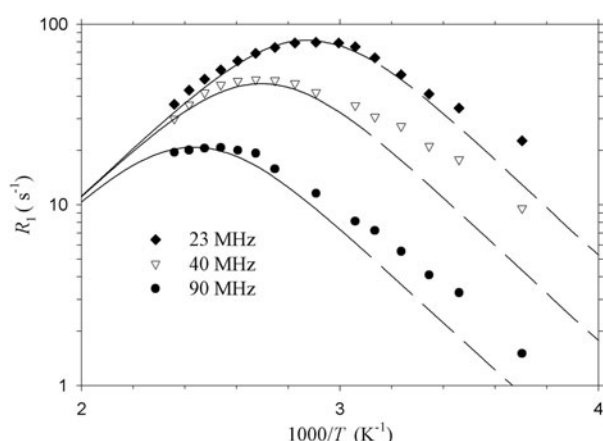


Figure 3. Proton relaxation rates R_1 in $\text{TaV}_2\text{H}_{0.1}$. Symbols are experimental data. The continuous lines are the calculated values for the temperature range 334–484 K. The dashed lines are the results assuming Arrhenius form of the diffusion data at lower temperatures.

calculations have assumed Arrhenius form for D and Γ_2 , with the range of temperature corresponding to the PFG-NMR data shown as continuous curves and the extrapolated region shown as dashed curves. The agreement with the experimental data is excellent at high temperatures and the calculated values are lower than the experimental values at lower temperatures.

The value of p to fit the value of the maxima is 0.7. Analysis of QENS data for TaV_2H_x for $x = 0.6$ and 1.1 suggested that H–H interactions lead to the formation of some ordered configurations at low temperatures and that this can lead to ‘static’ protons that do not participate in the fast localized motion (Skripov *et al* 1998) and would not contribute to the relaxation. If the fraction of such ‘static’ protons is $1 - p$ the effect on the relaxation rate is a multiplicative factor of p , as assumed in the above fitting procedure, if the proton magnetization is rapidly equalized by spin diffusion. The QENS study enabled estimates of the temperature dependence of p in the range 80–300 K. The value of p at 300 K is 0.6 and increases with temperature. This is in excellent agreement with the value of 0.7 obtained from the fit to the relaxation maximum at 344 K.

The value of the parameter A to fit the position of the 23 MHz maximum is 0.47. Without this adjustment the calculated relaxation maxima occur at values of $1000/T$ which are too large. This is typical of the behaviour for the BPP model, which is used here for the Γ_2 jumps. Accurate calculations of the spectral density functions for like-spin interactions and diffusion in cubic crystals show that the maxima of the relaxation rates occur at $\omega/\Gamma = 0.383$ (SC), 0.443 (BCC) and 0.474 (FCC) (Barton and Sholl 1980), compared with the BPP result of 0.62. The corresponding ratios to compare with A are therefore 0.62 (SC), 0.71 (BCC) and 0.76 (FCC), which decrease with coordination number of the structure. Diffusion away from a site will occur more rapidly for higher coordination numbers and so the BPP approximation will be better in such cases. The reason that the BPP model overestimates the jump rates is that it overestimates the rate at which the correlation function decays by assuming the correlation function becomes zero when a jump of a spin occurs. The decay is actually slower because spins in reality take a sequence of jumps to diffuse away which will reduce the rate of decay of the correlation function. While the above results for like-spin interactions are not directly comparable to the case of unlike-spin interactions for $\text{TaV}_2\text{H}_{0.1}$, the same effect of the BPP approximation overestimating the jump rates would be expected.

The calculated relaxation rates are lower than the experimental values on the low temperature side of the maximum in figure 3. The value of p also decreases with decreasing temperature so that this effect would reduce the calculated rate even further. A possible reason for this discrepancy is that the Arrhenius form of Γ_2 is not valid in this region. Analysis of the ultrasonic attenuation data in TaV_2H_x (Foster *et al* 2001) suggested that the H jump rate for low H concentrations shows an upward curvature on an Arrhenius plot for $1000/T$ greater than ~ 4 due to quantum diffusion. There is also a slight possible upward curvature of the diffusion data (Majer *et al* 1995) for $1000/T \sim 3$. An increase in the H jump rate from Arrhenius form would increase the calculated relaxation rates on the low temperature side of the maximum.

The other relaxation rate maxima (not shown) that occur at lower temperatures show appreciable asymmetry. As noted by Buzlukov and Skripov (2004) this asymmetry is inconsistent with a BPP model and Arrhenius temperature dependence of a jump rate. Buzlukov and Skripov proposed that the asymmetry was due to a non-Arrhenius jump rate arising from quantum diffusion behaviour of Γ_1 and deduced the temperature dependence of Γ_1 by fitting the experimental data. The present modification of the BPP model would use the spectral density function (13) to fit the low temperature relaxation data. This has not been calculated because no independent estimate of the jump rates is available in this temperature region. One feature of the low temperature maxima that can be used to check the validity of the present theory is the value of the maximum rate as this is independent of the temperature dependence of the jump rate. Only the 90 MHz data will be considered as the data for the other frequencies is probably influenced by cross-relaxation effects (Buzlukov and Skripov 2004). Comparing the experimental maximum rate at $T = 50$ K with the value calculated using the spectral density function (13) gives a value of $p = 0.06$ for the two to agree. This is consistent with $p \sim 0.08$ at 50 K obtained by extrapolating the $p(T)$ data obtained from the QENS data (Skripov *et al* 1998).

4. Nuclear spin relaxation in ZrCr_2H_x

The diffusion of H in ZrCr_2H_x has been studied by a range of methods. Proton spin relaxation data is available for $x = 0.2$ and 0.5 for resonant frequencies of 11, 19.3 and 90 MHz (Skripov and Belyaev 1993). The diffusivity of H has been measured by PFG-NMR for $x = 0.2$ and 0.5 (Renz *et al* 1994) and QENS data has been obtained for $x = 0.45$ (Skripov *et al* 1999). In addition, theoretical calculations of the jump rates of H in the low concentration limit using plane wave density functional theory have been made by Bhatia and Sholl (2005). These calculations used semiclassically corrected transition state theory to estimate contributions from tunnelling to each jump rate.

The spin relaxation data as a function of temperature shows a single asymmetric maximum at each frequency. This data can be fitted well by a BPP model with a Gaussian distribution of activation energies, but the parameters obtained from the fit are unsatisfactory (Skripov and Belyaev 1993).

The spin relaxation in this case is due to like-spin magnetic dipolar interactions between diffusing H since the metal nuclei with non-zero spin have low abundance. The relaxation rates R_1 are therefore given by equation (15). Values of the H jump rates and diffusivity have been calculated by Bhatia and Sholl (2005). The calculated jump rates for Γ_{eg} , Γ_{ge} , Γ_1 and Γ_2 are shown as a function of temperature in figure 4. Also shown are the corresponding values of the diffusivity and the experimental results from the PFG-NMR measurements (Renz *et al* 1994). The curvature in the Arrhenius plots is a consequence of quantum diffusion effects (Bhatia and Sholl 2005). The agreement between the theoretical and experimental D values is excellent except for a scaling factor. The proton spin relaxation rates are therefore calculated

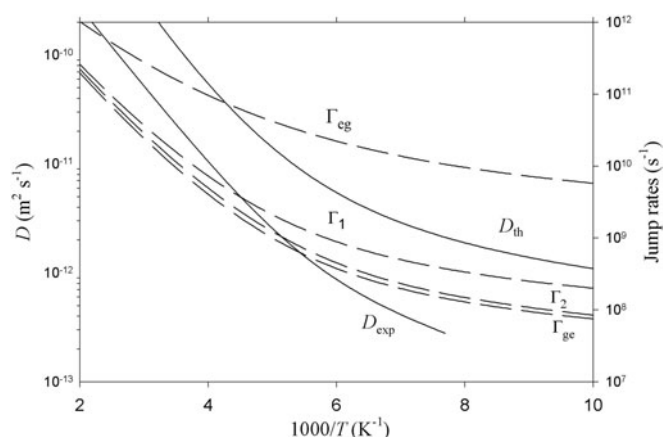


Figure 4. The calculated jump rates for H diffusion in ZrCr_2H_x (broken curves and right-hand scale). Also shown are the theoretical diffusivity D_{th} and the experimental diffusivity D_{exp} (continuous curves and left-hand scale.)

using scaled values of the jump rates. The scaling factor for the jump rates is a multiplicative temperature-dependent factor applied to all the jump rates that gives agreement between the theoretical and experimental values of D . The scaling factor at lower temperatures than those at which D was measured are assumed to be the same as the factor at $1000/T = 7.6$.

H in ZrCr_2H_x occupies mainly g sites with positional parameters $X = 0.066$ and $Z = 0.872$ (Skripov *et al* 1999). The occupation probabilities of the e and g sites can be deduced from the calculated values of $\Gamma_{\text{eg}}/\Gamma_{\text{ge}}$. The results are consistent with mainly g site occupation with, for example, $c_e/c_g = 0.013$ at $1000/T = 10$ and $c_e/c_g = 0.043$ at $1000/T = 4$. The effect of the small e site occupancy has been included in the relaxation rate calculations for completeness. The lattice sums S_i for the dipolar interactions are given in the table. The lattice parameter is $a = 7.26 \text{ \AA}$ (Skripov *et al* 1999). The values of the sums for H–H interactions are quite sensitive to the value of the minimum H–H separation. According to the Westlake criterion (see, for example, Flanagan and Oates 1988) the minimum separation of H in metals is $\sim 2.1 \text{ \AA}$. Results are given in the table for summations over all g sites (no restriction) and for minimum H–H separations of 2.0 and 2.1 \AA . The sensitivity of the values of the sums to the distance of closest approach of pairs of H implies that small changes in the structural parameters or local changes in the environment of H–H pairs could change the values of the sums significantly.

The calculated relaxation rates for H in $\text{ZrCr}_2\text{H}_{0.2}$ for 11 and 19.3 MHz are compared with the experimental data in figure 5. The theoretical results shown have used the lattice sums corresponding to a minimum H separation of 2.0 \AA , have been scaled by a factor $p = 0.74$ to fit the maximum experimental rate of 2.49 s^{-1} for the 19.3 MHz data, and the jump rates have been scaled by a factor of 0.5 to shift the curves to fit the position of the experimental maxima. The general behaviour of broad asymmetric maxima is well described by the calculations. The asymmetry in the maxima is related to the non-Arrhenius behaviour of the diffusivity, which is a consequence of the quantum diffusion effects at low temperatures shown by Bhatia and Sholl (2005).

The phenomenon of a fraction $1 - p$ of ‘static’ H described for TaV_2H_x in the previous section has also been observed for ZrCr_2H_x (Skripov *et al* 1999) by QENS. The value of p deduced from the QENS study was $p \sim 0.6$ at $T \sim 160 \text{ K}$. While this is reasonably consistent

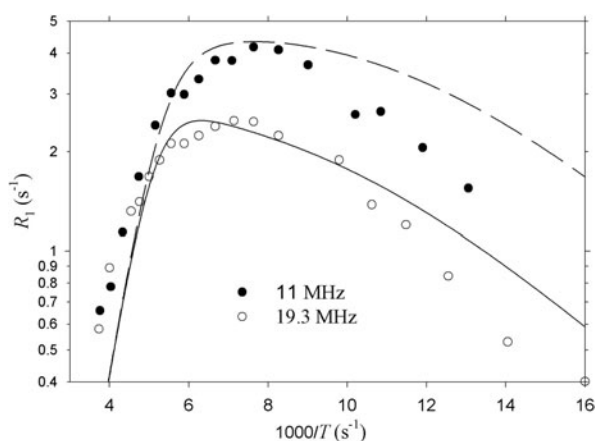


Figure 5. Proton relaxation rates R_1 in $\text{ZrCr}_2\text{H}_{0.2}$. Symbols are experimental data and the lines are the calculated values.

with the value of 0.74 deduced from the fit of the relaxation data, the uncertainties in the values of the sums S_i are significant. For example, using the set of sums with $r_{\min} = 2.1 \text{ \AA}$ results in a value of $p \sim 1$. The calculated relaxation rates are too small at high temperatures and too large at low temperatures. This behaviour is consistent with a temperature dependent fraction p that decreases with temperature.

The scaling of the jump rates by a factor of 0.5 to fit the position of the maxima in the relaxation rates is similar to the factor of 0.47 used for the case of TaV_2H_x . This effect is again likely to be a consequence of the use of the BPP approximation for H jumps other than those within hexagons. The general features of the relaxation rates are therefore well described by the theory.

5. Conclusions

The BPP model for nuclear spin relaxation for diffusion between e and g sites has been modified to include an accurate description of jumps between g sites within hexagons. This enables more accurate analysis of experimental relaxation rates for interstitial diffusion in the C15 AB_2 structure, especially for cases where there are rapid jumps within hexagons. The analysis could also be extended to other systems such as the C14 structure. The BPP model is still used in the present theory for jumps between hexagons and jumps including e sites. One consequence of this approximation is that jump rates deduced from fitting relaxation data will be too large by typically a factor of two.

The analysis of the proton relaxation data for $\text{TaV}_2\text{H}_{0.1}$ and $\text{ZrCr}_2\text{H}_{0.2}$ has shown that the relaxation rates are consistent with low temperature quantum diffusion, the existence of a temperature-dependent fraction of ‘static’ protons, and H interaction effects that prevent H approaching each other too closely. The effect and details of these phenomena cannot be deduced solely by the use of nuclear spin relaxation data. However, the combination of the relaxation data with information from diffusivity measurements, QENS analysis and theoretical calculations can reveal considerable detail about the microscopic nature of H diffusion. The examples considered in this paper show that these different approaches can yield consistent results.

References

- Abragam A 1961 *The Principles of Nuclear Magnetism* (Oxford: Clarendon)
- Barton W A and Sholl C A 1980 *J. Phys. C: Solid State Phys.* **13** 2579
- Bhatia B, Luo X, Sholl C A and Sholl D S 2004 *J. Phys.: Condens. Matter* **16** 8891
- Bhatia B and Sholl D S 2005 *Phys. Rev. B* at press
- Bloembergen N, Purcell E M and Pound R V 1948 *Phys. Rev.* **73** 679
- Buzlukov A L and Skripov A V 2004 *J. Alloys Compounds* **366** 61
- Eberle U, Majer G, Skripov A V and Kozhanov V N 2002 *J. Phys.: Condens. Matter* **14** 153
- Fischer P, Fauth F, Skripov A V, Podlesnyak A A, Padurets L N, Shilov A L and Ouladdiaf B 1997 *J. Alloys Compounds* **253/254** 282
- Flanagan T B and Oates W A 1988 *Top. Appl. Phys.* **63** 49
- Foster K, Hightower J E, Leisure R G and Skripov A V 2001 *J. Phys.: Condens. Matter* **13** 7327
- Lichty L, Han J W, Ibanez-Meier R, Torgeson D R, Barnes R G, Seymour E F W and Sholl C A 1988 *Phys. Rev.* **39** 2012
- Majer G, Renz W, Seeger A, Barnes R G, Shinar F and Skripov A V 1995 *J. Alloys Compounds* **231** 220
- Renz W, Majer G, Skripov A V and Seeger A 1994 *J. Phys.: Condens. Matter* **6** 6367
- Sholl C A 1993 *Defect Diffus. Forum* **95-98** 91
- Sholl C A 2005 *J. Phys.: Condens. Matter* **17** 1329
- Skripov A V 2004 *Defect Diffus. Forum* **224/225** 75
- Skripov A V and Belyaev M Y 1993 *J. Phys.: Condens. Matter* **5** 4767
- Skripov A V, Cook J C, Sibirtsev D S, Karmonik C and Hempelmann R 1998 *J. Phys.: Condens. Matter* **10** 1787
- Skripov A V, Pionke M, Randl O and Hempelmann R 1999 *J. Phys.: Condens. Matter* **11** 1489