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LETTER TO THE EDITOR

Nuclear spin relaxation by translational diffusion of hydrogen in BCC metals: the effect of hopping to second-nearest neighbours

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Abstract. Quantities relevant to the theoretical determination of D/T_1 are calculated, where D is the tracer diffusion coefficient and T_1 is the spin–lattice relaxation time for relaxation due to magnetic dipolar coupling between diffusing hydrogen spins. Calculations are performed for hydrogen spins diffusing on the tetrahedral interstitial sites of a BCC host metal and both the like-spin (hydrogen–hydrogen) and unlike-spin (metal–hydrogen) contributions are determined. The Monte Carlo/analytic method devised by Faux, Ross and Sholl is used. Results are obtained for the hydrogen-to-metal ratio of 0.6 for a multiple-site-blocking model in which the hydrogen spins block all sites to either the second or the third neighbour. A fraction F_2 of hops are assumed to occur to second-nearest-neighbour sites. Agreement is obtained for the first time with the experimental result on $\text{NbH}_{0.6}$ with $F_2 > 0.6$.

Nuclear magnetic resonance has proved to be an effective probe of the diffusional properties of hydrogen absorbed in a variety of metals. It is convenient to measure the quantity D/T_1 where D is the tracer diffusion coefficient and T_1 is the overall characteristic relaxation time. The present letter focuses on the Nb/H system where there are three main contributions to T_1 , one due to the relaxation caused by hydrogen spins diffusing relative to each other, the second due to hydrogen spins diffusing relative to spin-bearing stationary nuclei and the third due to the interaction of spins with conduction electrons. The second of these is the most important in the Nb/H system as the most abundant isotope of Nb has a spin of $5/2$. The component due to the interaction with conduction electrons can be subtracted out of the experimental results via the Korringa relationship. Other possible contributors to T_1 , such as that due to paramagnetic impurities, are assumed to be negligible. The remaining quantity, the tracer diffusion coefficient D , is proportional to the slope of the relaxation rate curve at high temperatures (or low frequencies) and is equal to $\langle l^2 \rangle f / 6\tau$, where $\langle l^2 \rangle$ is the mean square jump distance of the spin, f is the tracer correlation factor and τ is the mean time between successive hops of a spin.

The experimental measurements of D/T_1 are usually compared with theoretical models which make various simplifying assumptions concerning the nature of the diffusion of hydrogen spins. The BPP model due to Bloembergen *et al* (1948) is probably the most widely used for comparison with experimental results. It was originally developed as a model for liquids but has found frequent use in the analysis of solid-state

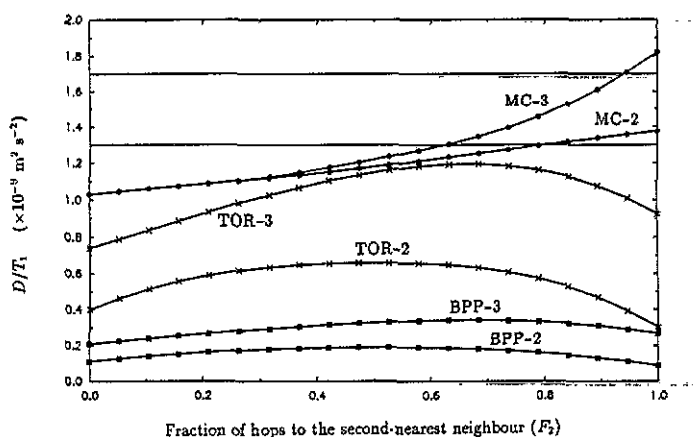


Figure 1. D/T_1 plotted as a function of F_2 . The Monte Carlo results are indicated for blocking to the second-nearest neighbour (MC-2) and the third-nearest neighbour (MC-3). The experimental result of Zogal and Cotts, $1.5 \pm 0.2 \times 10^{-9} \text{ m}^2 \text{ s}^{-2}$, is represented by the two full curves. The results from the BPP model (BPP-2 for blocking to the second-nearest neighbour and BPP-3 blocking to the third-nearest neighbour) and the Torrey model (TOR-2 and TOR-3) are also indicated.

diffusion problems. This theory has significant shortcomings, however, for some solid-state systems, including Nb/H.

The BPP theory has been superseded over the years by theories due to a number of workers, notably Torrey (Torrey 1953, Resing and Torrey 1963), Sankey and Fedders (Sankey and Fedders 1980) and Faux and co-workers (Faux *et al* 1986, Faux and Hall 1988, 1989). Each theory differs in accuracy and mathematical complexity. For the case of hydrogen diffusion in BCC metals it has been shown, however, that the Monte Carlo/analytic technique is the only one capable of obtaining accurate results at arbitrary interstitial concentrations and for the site-blocking model (Faux and Hall 1989).

The Monte Carlo/analytic technique involves the explicit determination of the pair correlation functions using a Monte Carlo calculation when the separation between pairs of spins is small, whilst the contribution to the relaxation rate due to diffusion over larger distances and longer times is accounted for using a continuum model. Final relaxation rates are generally accurate to within a few percent, although the method is least accurate in the high-frequency (low-temperature) regime or at very low or very high interstitial concentrations (less than 1% or at the monovacancy limit).

The focus in this letter is on the diffusion of hydrogen in BCC metals, particularly Nb. In Nb/H the hydrogen spins occupy the tetrahedral interstitial sites. There are twelve sites per unit BCC cell with four sites on each face (see Faux and Ross (1987), figure 1). Each hydrogen spin has four nearest-neighbour sites and two second-nearest-neighbour sites. Furthermore, it is generally assumed that each hydrogen spin prevents the occupation of neighbouring sites to a distance corresponding to either the second- or third-nearest neighbour (Faux and Ross (1987) and references therein). The site-blocking models appear to give a good representation of the diffusional behaviour of hydrogen in Nb with the effective blocking distance between the second and third neighbour. The site-blocking model is retained in the present work.

To date no theoretical model has obtained agreement with the experimental value for D/T_1 obtained by Zogal and Cotts (1975) for $\text{NbH}_{0.6}$. In the original paper, Zogal

and Cotts compared their results using the BPP model and concluded that agreement could only be obtained if the interstitials made a significant proportion of jumps to non-nearest-neighbour sites. In other words, the theoretical value of D/T_1 would be raised if the value of $\langle l^2 \rangle$ was increased. Zogal and Cotts estimated that $\langle l^2 \rangle^{1/2}$ would need to correspond to a distance of between the second and fifth neighbour. This analysis, however, was based on the BPP theory which has been shown to be inaccurate for this system. A calculation by Faux and Hall (1989), hereafter referred to as FH, achieved closer agreement with the experimental value but the theoretical result was still too small by a factor 1.5. It was stated by FH that agreement could be obtained if it was assumed that roughly 50% of the hops were to nearest-neighbour sites and 50% to second-nearest-neighbour sites. This is not strictly true as there are four important factors that determine the high-temperature slope of the relaxation rate curve. This may be seen by combining equations (11) and (12) from FH to give the expression for D/T_1 :

$$D/T_1 = (\langle l^2 \rangle f / 6) (Ag(0) + \frac{2}{3} Bh(0)) \quad (1)$$

where the constants A and B are $2.672 \times 10^7 \text{ s}^{-2}$ and $5.250 \times 10^8 \text{ s}^{-2}$ respectively for the Nb/H system. The four important factors that determine the high-temperature slope of the relaxation rate curve are therefore $\langle l^2 \rangle$, the mean square jump distance, f , the tracer correlation factor, $g(0)$, the total area under the curve of the like-spin correlation function, and $h(0)$, the total area under the curve of the unlike-spin correlation function. All four quantities must be calculated for a specific diffusion model in order to obtain accurate theoretical predictions for D/T_1 .

The calculations of FH are modified in this letter to allow a proportion of hops to second-nearest-neighbour sites. By examining the positions of the interstitial sites in space it appears that the activation energy for hops to either first- or second-nearest-neighbour sites is likely to be lower than that for hops to more distant sites which are partially restricted by the positions of metal atoms. A model that assumes that a proportion of hops are made to the second-nearest-neighbour sites in BCC crystals will indeed increase the value of $\langle l^2 \rangle$ as the mean jump distance is larger. However, f , $g(0)$ and $h(0)$ also change. In the case of the BCC crystal, there are only two second-nearest-neighbour sites compared to four first nearest-neighbour sites, and so the effective coordination number is reduced as the proportion of jumps to second-nearest-neighbour sites increases. The value of f is therefore reduced as successive hops of the interstitials become more correlated. This counteracts the increase in $\langle l^2 \rangle$. The increased correlation in the diffusive motion of the spins is also apparent in the values of $g(0)$ and $h(0)$. Each spin spends a larger proportion of time in the vicinity of neighbouring spins and neighbouring nuclei, and so the values of $g(0)$ and $h(0)$ increase.

In this letter, the values of $\langle l^2 \rangle$, f , $g(0)$ and $h(0)$ are calculated for the diffusion of hydrogen spins on the tetrahedral sites of a BCC crystal. Blocking of sites to the second-nearest neighbour and the third-nearest neighbour is assumed and a fraction F_2 of hops are assumed to occur to the second-nearest-neighbour sites. The hopping rate to first-nearest-neighbour sites and second-nearest-neighbour sites is therefore proportional to $1 - F_2$ and F_2 respectively.

Details of the Monte Carlo procedure and the accompany calculations required for the determination of D/T_1 have been published (Faux *et al* 1986, FH) and so will not be repeated here. The calculations presented in this letter are based on those of FH, with the modification that a certain fraction F_2 of hops are to the second-nearest-neighbour sites. As in FH, each interstitial is assumed to block all sites to either the second- or the

Table 1. The quantities required for the calculation of D/T_1 using equation (1) for different values of F_2 .

Blocking	F_2	$\langle l^2 \rangle^{1/2}$	f	$g(0)$	$h(0)$	D/T_1
2	0.00	1.414	0.78	2800	1330	1.03
	0.10	1.473	0.830	2434	1200	1.06
	0.25	1.561	0.848	2140	1090	1.10
	0.50	1.714	0.823	1900	1090	1.22
	0.75	1.845	0.728	1930	1190	1.41
	0.90	1.927	0.609	2260	1510	1.62
3	0.00	1.414	0.44	4280	2410	1.03
	0.10	1.473	0.517	3301	1967	1.06
	0.25	1.566	0.542	2770	1740	1.10
	0.50	1.714	0.487	2720	1730	1.18
	0.75	1.859	0.375	3170	2080	1.28
	0.90	1.944	0.268	4210	2790	1.34

third-nearest neighbour. All calculations are for a hydrogen-to-metal ratio of 0.6. The values of $\langle l^2 \rangle$, f , $g(0)$ and $h(0)$ are evaluated using the Monte Carlo procedure and are listed in the table for each site-blocking model. Results for $F_2 = 0$ have already been published (FH) and are included in the table for completeness.

The values of D/T_1 for each site-blocking model are displayed in figure 1 as a function of F_2 . The curves are obtained by fitting a cubic spline to the values presented in the table. The curves rise due to the increased value of $\langle l^2 \rangle$, but not as steeply as would be expected if the increase in $\langle l^2 \rangle$ were the only factor involved in the evaluation of D/T_1 . The experimental value of $1.5 \pm 0.2 \times 10^{-9} \text{ m}^2 \text{ s}^{-2}$ is indicated in the figure. If blocking to the second-nearest neighbour is assumed, agreement with the experimental result is obtained if $F_2 > 0.8$. If blocking to the third-nearest neighbour is assumed, agreement with the experimental result is obtained if $0.6 < F_2 < 0.95$. As the diffusional properties of H in Nb are most successfully described by a blocking distance between the second-nearest neighbour and third-nearest neighbour (Faux and Ross 1987), it may be concluded that agreement with the experimental result is obtained if $F_2 > 0.6$.

It is also possible to compare the experimental result with the Torrey and BPP models. In the BPP model, $g(0) = 319.2$ and 158.5 for site blocking to the second- and third-nearest neighbour respectively and $h(0) = 293.1$. The values of $\langle l^2 \rangle$ and f are those presented in the table. The BPP curves are displayed in the figure and are too low for either blocking model and for all values of F_2 . For the Torrey model, $g(0) = 1917$ and 1476 for site blocking to the second- and third-nearest neighbour respectively and $h(0) = 963.6$ for both blocking models. Again, the values of $\langle l^2 \rangle$ and f are those presented in the table. The Torrey model is a considerable improvement over the BPP model, but still the values are too low and agreement is not possible even to within the large experimental error.

There is no straightforward method of modifying the multiple-scattering theory of Sankey and Fedders (1980) as this theory has not been formulated for the site-blocking models.

In conclusion, there are four important factors that determine the high-temperature slope of the relaxation rate curve. These are $\langle l^2 \rangle$, the mean square jump distance, f , the tracer correlation factor, $g(0)$, the total area under the curve of the like-spin correlation function, and $h(0)$, the total area under the curve of the unlike-spin correlation function.

These quantities are calculated using the Monte Carlo/analytic method of Faux, Ross and Sholl for the $\text{NbH}_{0.6}$ system. Agreement with the experimental result of Zogal and Cotts (1975) is obtained for the first time if the fraction of second-nearest neighbour hops exceeds 0.6.

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