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## Nuclear spin relaxation due to the translational diffusion of hydrogen in BCC metals

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**Abstract.** We calculate the spectral density functions required for the theoretical determination of nuclear spin relaxation rates due to magnetic dipolar coupling between diffusing hydrogen spins in BCC metals. Both the like-spin (hydrogen–hydrogen) and unlike-spin (metal–hydrogen) contributions are determined using the Monte Carlo method of Faux, Ross and Sholl. Results are obtained for hydrogen-to-metal ratios of 0.12, 0.3 and 0.6 for the simple hopping model (no multiple occupancy of sites) and for a multiple site-blocking model in which the hydrogen spins block all sites as far as the second or third neighbour. For the simple hopping model, the results are in very good agreement with the multiple-scattering theory of Sankey and Fedders in the high- and low-temperature limits. For the multiple site-blocking models, it is found that the BPP model (due to Bloembergen, Purcell and Pound) and Torrey model can differ significantly from the Monte Carlo result, particularly at higher concentrations. The results obtained for  $D/T_1$ , where  $D$  is the tracer diffusion coefficient and  $T_1$  is the spin–lattice relaxation time, are compared to the experimental result on  $\text{NbH}_{0.6}$ . The Monte Carlo method gives a value which is  $\frac{2}{3}$  of the experimental value if blocking to either the second or the third neighbour is assumed. Agreement with experiment may be obtained if it is assumed that the hydrogen diffuses by a combination of jumps to nearest-neighbour and second-nearest-neighbour sites.

### 1. Introduction

There are a number of BCC metals which can absorb appreciable quantities of hydrogen, notably niobium, tantalum and vanadium. The hydrogen is highly mobile and diffuses by making thermally activated hops from one interstitial site to another. The type of interstitial site occupied by the hydrogen was the subject of dispute in early years but, in Nb and Ta at least, it has been established that the hydrogen occupies primarily the tetrahedral interstitial sites. There are four tetrahedral interstitial sites on each face of the BCC unit cell located at the  $(\frac{1}{2} \frac{1}{4} 0)$  position. Although there are 6 interstitial sites per metal atom available for hydrogen atom occupancy, experimentally one finds that the fraction of interstitial sites,  $c$ , saturates at a maximum attainable concentration of  $c \approx \frac{1}{6}$ . This suggests that a hydrogen atom occupying one site reduces the occupation probability of neighbouring sites for other hydrogens. This is not surprising because the distance between neighbouring interstitial sites is rather small (about 1.2 Å in Nb). It is convenient to adopt a model which assumes that each hydrogen blocks completely all sites to either

the second or third neighbour and to neglect all longer-range interactions. We refer to this as the multiple site-blocking model.

The multiple site-blocking model has been used successfully to explain many of the thermodynamic and diffusive properties of hydrogen in BCC metals. Oates *et al* (1985), for instance, undertook a series of Monte Carlo calculations of a variety of thermodynamic quantities and concluded that the effective blocking distance decreased from third to second neighbour as the temperature increased. A similar conclusion was reached by Faux and Ross (1987) who examined the tracer diffusion coefficients at different temperatures and concentrations in Nb/H and Ta/H, as obtained by NMR and quasielastic neutron scattering. These observations have recently been confirmed by some detailed quasielastic neutron scattering studies of deuterons in Nb (Hempelmann *et al* 1988). It appears therefore that many of the properties of hydrogen in Nb and Ta are well described by a multiple site-blocking model and for this reason, and also for the ease with which it may be incorporated into a Monte Carlo simulation, we have adopted this model in the present paper.

Much of the experimental work on metal-hydrogen systems has been directed toward the measurement of transport-related quantities such as the tracer diffusion coefficient, mean residence time, jump length (the hydrogen may not necessarily hop to nearest-neighbour sites), activation energies for diffusion and the pre-exponential factors. NMR has proved to be one of the most popular techniques for the evaluation of these quantities. Direct determination of the tracer diffusion coefficient combined with spin-lattice relaxation rate ( $T_1^{-1}$ ) measurements can lead to estimations of all the above quantities. Measurements of the relaxation rate are only useful however, if the experimental data can be compared to an appropriate theory.

There are four different theories which have been used to determine the relaxation rate for a system of diffusing spins occupying the tetrahedral site of a BCC host; each contains different levels of approximation. The simplest of these is the BPP theory, named after Bloembergen, Purcell and Pound (1948), and sometimes called the single-relaxation-time (SRT) theory. Despite being derived for liquids, it has found frequent use in solid-state systems and has the advantage that the final relaxation rate is of a simple analytic form. Each of the remaining theories produces approximate results based on the simple hopping model (no multiple occupancy of sites) but none addresses explicitly the problem of multiple site-blocking. The second theory, due to Torrey (1953), represents the first attempt to treat the discrete nature of lattice diffusion (see also Resing and Torrey 1963 and Weaver and Van Dyke 1972). This theory assumes that a spin may hop to any position on the surface of a sphere of radius  $l$  from its current position. The theory is a significant improvement over the BPP model and it is fairly straightforward to evaluate the integrals required for the determination of the spectral density functions and hence the relaxation rate. The Torrey theory is most accurate for lattices with high coordination numbers, such as the FCC lattice which has 12 nearest neighbours, and is least accurate for lattices with low coordination such as that of interest here. The third theory, the multiple-scattering (MS) theory of Sankey and Fedders (1980), is easily the most accurate of the three so far described producing values of the relaxation rate which are estimated to be accurate to within a per cent or so. The MS theory is the only theory which determines explicitly the spin-spin correlation functions and is therefore the only theory which predicts different values of the relaxation rate at different concentrations (although it is possible to make some crude modifications to the BPP and the Torrey theories). The MS theory is, however, highly complex and it is not possible to present analytic expressions for the relaxation rate. Sankey and Fedders

do, however, evaluate the high- and low-temperature limits and these are useful for comparison to the present results. The fourth theory is by MacGillivray and Sholl (1983) who evaluate the low-temperature limit of the relaxation rate using mean-field theory. Their results are exact as the spin concentration vanishes.

It should be emphasised that the theories outlined above are concerned only with the simple hopping model. Yet even for this simple model an exact determination of the relevant diffusion correlation functions at arbitrary concentrations is not possible. Each of the theoretical methods tackles this simple case to various degrees of approximation. We, however, are concerned with the effects of multiple site-blocking on the relaxation rate. This problem is even more complicated and can only be introduced into the above theories in a very approximate way. It is clear that only a Monte Carlo method is capable of accurately determining the appropriate diffusion correlation functions and hence the relaxation rate for the multiple site-blocking model.

The first attempt at using a Monte Carlo (MC) method to evaluate the diffusion correlation functions necessary to determine relaxation rates was made by Bustard (1980), but his work was specifically geared towards the Ti/H system. The only other MC studies of the relaxation rate are those of Faux, Ross and Sholl (1986), hereafter referred to as FRS, and the follow-up study by Faux and Hall (1988). FRS calculated the like-spin relaxation rate for spins diffusing on the BCC, FCC and SC lattices using the simple hopping model. These authors evaluated the correlation functions using a MC method for short diffusion distances (which require an accurate determination of the correlation functions) and an analytic correction, based on the diffusion equation, at longer distances. Special methods were also used in the Fourier transform process required to produce the final relaxation rates. Faux and Hall (1988), hereafter referred to as FH, demonstrated the flexibility of the MC method by investigating the effect of nearest-neighbour interactions between diffusing spins on  $T_1^{-1}$ . They showed that a finite interaction energy could lead to asymmetries in the peak of the relaxation rate. The MC procedure introduced by FRS and modified by FH produces results which are estimated to be accurate to better than 2%, except at high frequencies (low temperatures) when the Fourier transform procedure becomes less accurate. FH also introduced a convenient method of expressing the results by fitting an expression of the form suggested by Sholl (1988) to the MC data.

In this paper the MC method introduced by FRS and modified by FH will be used to evaluate the diffusion correlation functions and hence the spectral density functions for hydrogen spins diffusing via nearest-neighbour hops between the tetrahedral interstitial sites of a BCC host metal. The calculations are performed for the simple hopping model and also for the cases where each hydrogen atom blocks sites out to the second or third nearest neighbour. Results are obtained at the atomic ratios  $x = 0.12, 0.3$  and  $0.6$  where  $x = 6c$ .

The calculation is outlined in the following section. The results are presented in section 3 and are compared to the predictions of the BPP, Torrey and MS theories and also to the experimental result on  $\text{NbH}_{0.6}$ . Finally, the conclusions are presented in section 4.

## 2. Calculation

The spectral density functions calculated in the present paper may be used to determine the spin-lattice relaxation rate ( $T_2^{-1}$ ) or the spin-lattice relaxation rate in the rotating

frame ( $T_{1\rho}^{-1}$ ). We shall concentrate on the  $T_1^{-1}$  relaxation rate.  $T_1^{-1}$  usually consists of three components

$$T_1^{-1} = T_{\text{II}}^{-1} + T_{\text{IS}}^{-1} + T_e^{-1} \quad (1)$$

The quantity  $T_e^{-1}$  is the contribution to the relaxation due to the interaction of spins with conduction electrons. This portion is generally assumed to be described by the well known Korringa relation and is subtracted from the experimentally determined relaxation rate. The remaining terms,  $T_{\text{II}}^{-1}$  and  $T_{\text{IS}}^{-1}$ , can be determined from the spectral density functions calculated in the present paper.  $T_{\text{II}}^{-1}$  is the relaxation rate due to the like-spin (hydrogen–hydrogen) dipolar interactions and  $T_{\text{IS}}^{-1}$  is the contribution due to unlike-spin (hydrogen–metal) dipolar interactions. If the metal has no nuclear spin ( $S = 0$ ), the latter contribution is zero. For the case of Nb,  $S$  is equal to  $\frac{5}{2}$  and so the unlike-spin component is an important contribution to the relaxation rate.

Each relaxation rate may be expressed in terms of the spectral density functions  $g(y)$  and  $h(y)$  by the following equations (Abragam 1961, Cotts 1972, Sholl 1974),

$$T_{\text{II}}^{-1} = \frac{1}{5}A\tau[g(y) + 4g(2y)] \quad (2)$$

$$T_{\text{IS}}^{-1} = \frac{1}{5}B\tau[\frac{1}{3}h(y - Wy) + h(y) + 2h(y + Wy)] \quad (3)$$

where  $\tau$  is the mean residence time of a hydrogen spin at an interstitial site. The dimensionless quantities  $y$  and  $W$  are equal to  $\omega_1\tau/2$  and  $\omega_S/\omega_1$  respectively, where  $\omega_1$  and  $\omega_S$  are the Larmor frequencies of the hydrogen and metal nuclei. The expressions for  $A$  and  $B$  are,

$$A = (\mu_0/4\pi)^2\gamma_1^4\hbar^2I(I+1)cb^{-6} \quad (4)$$

$$B = (\mu_0/4\pi)^2\gamma_1^2\gamma_S^2\hbar^2S(S+1)Qb^{-6} \quad (5)$$

where  $\gamma_1$ ,  $\gamma_S$ ,  $I$  and  $S$  are the gyromagnetic ratios and spin quantum numbers of the proton and metal nucleus respectively. The quantities  $c$  and  $Q$  are, respectively, the fraction of interstitial sites containing a hydrogen spin and the fraction of metal nuclei which possess a spin ( $Q = 1$  if all metal isotopes possess the spin  $S$ ).  $b$  is the cubic lattice parameter of the metal lattice. The remaining term, the permeability of the vacuum  $\mu_0$  divided by  $4\pi$ , is included to ensure that equations are correct with all quantities in SI units.

In this paper we focus on the calculation of the spectral density functions  $g(y)$  and  $h(y)$  for hydrogen spins diffusing via the tetrahedral sites of a BCC metal. In equations (2) and (3), the lattice summations which normally appear in expressions of this type (see for example Cotts 1972) are incorporated within  $g(y)$  and  $h(y)$ . This can be seen in equations (6)–(9) which relate these functions to the fundamental probabilities describing the diffusion of the spins. The spectral density functions are the Fourier transforms of the correlation functions  $G_I^*(u)$  and  $G_S^*(u)$ ,

$$g(y) = 2 \int_0^\infty G_I^*(u) \cos(2yu) du \quad (6)$$

$$h(y) = 2 \int_0^\infty G_S^*(u) \cos(2yu) du \quad (7)$$

where the dimensionless quantity  $u$ , equal to  $t/\tau$ , is the average number of jumps per atom and is a convenient time scaling for the Monte Carlo program. The Monte Carlo calculations are performed for values of  $u$  ranging from 0 to a maximum value  $u_m$ , which

is chosen to be 18. For  $u > u_m$ , the correlation functions are approximated by an expression of the form  $Cu^{-3/2}$  where  $C$  is easily evaluated (FH). For  $u \leq u_m$ , the following expressions are used to evaluate the correlation functions (FH),

$$G_I^*(u) = b^6 \sum_i \sum_j^{r_i=r_j=r_{\max}} P_2(\cos \theta_{ij}) P_I(r_i, r_j, u) \frac{P'(r_i)}{c} r_i^{-3} r_j^{-3} + G_c^*(u, \Omega_I, 2D) \quad (8)$$

$$G_S^*(u) = b^6 \sum_m \sum_n^{r_m=r_n=r_{\max}} P_2(\cos \theta_{mn}) P_S(r_m, r_n, u) r_m^{-3} r_n^{-3} + G_c^*(u, \Omega_S, D) \quad (9)$$

$P_I(r_i, r_j, u)$  is the probability that a pair of hydrogen spins, separated by  $r_i$  at time zero, are separated by  $r_j$  at time  $u$ . Similarly,  $P_S(r_m, r_n, u)$  describes the motion of a hydrogen spin relative to the metal nuclei. These probability functions are fundamentally different and each has to be determined from the Monte Carlo simulation.  $P_I$  describes the relative motion of pairs of spins which occupy the same lattice but cannot, of course, occupy the same interstitial site or diffuse through each other.  $P_S$ , on the other hand, describes the motion of a mobile spin relative to a stationary metal nucleus which does not interfere with the motion of the mobile spin. Both these functions are calculated by the Monte Carlo program to a maximum pair separation  $r_{\max}$  which, in all simulations, included all pairs separated by a distance of up to the thirteenth neighbour.

A second probability function,  $P'(r_i)$ , is also evaluated by the Monte Carlo program. This is the average spin concentration in a shell of radius  $r_i$  about a hydrogen spin.  $P'(r_i)/c$  is unity for the simple hopping model at all values of  $r_i$  but differs from unity for the multiple site-blocking models. The equivalent term in equation (9) is always equal to one, even in the presence of multiple blocking, and so is omitted. The second Legendre polynomial  $P_2(x)$  is equal to  $\frac{1}{2}(3x^2 - 1)$  and  $\theta_{ij}$  (or  $\theta_{mn}$ ) is the angle between the vectors  $r_i$  and  $r_j$  (or  $r_m$  and  $r_n$ ).

The like-spin correction term  $G_c^*$  in equation (8), which accounts for pairs separated by  $r > r_{\max}$ , is identical to that used in a previous publications (FRS equation 3.2) but has been written here to be a function of the volume per hydrogen site  $\Omega_I$  and the tracer diffusion coefficient  $D$  as well as the time  $u$ . The correction term for unlike-spin hopping has the same functional form as the correction term for like-spin hopping except that the volume per metal site  $\Omega_S$  is used and  $D$  is replaced by  $\frac{1}{2}D$ . The latter is necessary because the correction term derived in FRS was developed for two spins each moving with a diffusion coefficient  $D$  whereas, for the unlike-spin contribution, the hydrogen spins are moving with a diffusion coefficient  $D$  relative to stationary metal nuclei.

The entire procedure may be summarised as follows. First the Monte Carlo simulation determines the probability functions  $P_I$ ,  $P_S$  and  $P'$  using the same procedures as described by FRS and FH. The simulations were performed on a lattice of 210912 hydrogen sites for  $x = 0.12$  and 127776 hydrogen sites at the remaining concentrations. In each run, a series of measurements are made at various intervals of  $u$  from 0 to 18 ( $u_m$ ) jumps per atom. Typically several hundred such runs are required to obtain satisfactory statistics. It is difficult to generate results at smaller concentrations than the value 0.12 used here because larger lattice sizes would be needed. The results for the probability functions are substituted into equations (8) and (9) and the correction term is added to obtain the correlation functions  $G_I^*$  and  $G_S^*$ . These correlation functions are dependent only on the time parameter  $u$ . Special Fourier transform techniques (fully described in FRS and FH) are then used to evaluate the spectral density functions.

**Table 1.** The parameters required to determine  $g(y)$  via equation (10) are presented.  $A_1$ ,  $A_2$  and  $A_3$  are fit to the data. The results are presented as a function of the hydrogen-to-metal ratio  $x$  for the simple hopping model (model 0) and for multiple site-blocking to the second (model 2) and third (model 3) neighbour.

Model	$x$	$g(0)$	$C$	$A_1$	$A_2$	$A_3$
0	0.12	6520	563	0.051	0.197	1550
	0.3	6580	578	0.060	0.168	1520
	0.6	6690	596	0.061	0.202	1550
2	0.12	2300	597	0.071	-0.198	65.3
	0.3	2460	663	0.069	-0.147	68.9
	0.6	2800	801	0.065	-0.082	70.8
3	0.12	2000	651	0.035	-0.036	25.5
	0.3	2380	861	0.026	0.216	32.9
	0.6	4280	1904	0.002	0.608	34.4

### 3. Results and discussion

The spectral density functions  $g(y)$  and  $h(y)$  are evaluated at three hydrogen concentrations  $x = 0.12, 0.3$  and  $0.6$ . At each of these concentrations, results are obtained for the simple hopping model and also for the multiple site-blocking model with the blocking extending to either the second neighbour or to the third neighbour. Each interstitial site has four first, two second and eight third nearest neighbours.

The MC results are fitted to expressions for  $g(y)$  and  $h(y)$  which have the correct functional form in the small- $y$  and large- $y$  limits for both  $g(y)$  and  $h(y)$ . The expression is that used by FH which was based on a form suggested by Sholl (1988), namely,

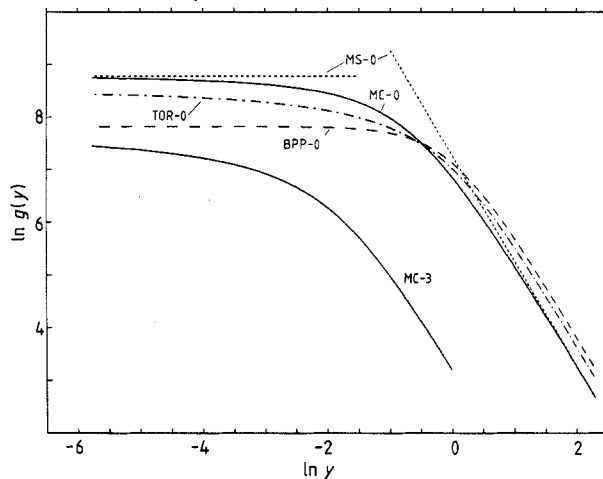
$$g(y) = [g(0)^{-1} + (4\pi^{1/2}C/g(0)^2)y^{1/2} + (A_1y^{3/4} + A_2y^{3/2} + y^2)/A_3]^{-1} \quad (10)$$

with a similar expression for  $h(y)$ . The parameters which are fit to the data ( $A_1$ ,  $A_2$  and  $A_3$ ) are presented in tables 1 and 2 together with the remaining quantities necessary to generate  $g(y)$  and  $h(y)$  using equation (10). The value of  $C$  in these tables is obtained using equation (10) of FH with values of the tracer correlation factor obtained from the expressions of Faux and Ross (1987). (Note that equation (10) of FH has the quantity  $u$  incorrectly included). Good fits are obtained to all data up to a maximum value of  $y$  of 10 for the simple hopping model. With blocking extending to the second and third neighbour, the maximum value of  $y$  used for the fits was 5 and 1 respectively. At larger values of  $y$  the data are poor due to the increasingly significant contribution which comes from the numerical part of the Fourier transform.

In figure 1, the MC values for  $g(y)$  at  $x = 0.12$  are presented for the simple hopping model (labelled MC-0) and the third-neighbour blocking model (labelled MC-3). The MC values for the simple hopping model are compared to the BPP (Bloembergen, Purcell and Pound 1948) and Torrey (Torrey 1953, Resing and Torrey 1963, Weaver and Van Dyke 1972) theories and also with the MS theory (Sankey and Fedders 1980) at the small- and large- $y$  limits. (MacGillivray and Sholl also evaluated the large- $y$  limit using mean-field theory and obtained a similar result to Sankey and Fedders). The BPP and the Torrey models are expected to be most accurate in the limit  $x \rightarrow 0$ . The MS theory is exact in this limit, but only the small and large- $y$  extrema are published by Sankey and Fedders. The

**Table 2.** The parameters required to determine  $h(y)$  using an expression similar to equation (10) are presented.  $A_1$ ,  $A_2$  and  $A_3$  are fit to the data. The results are presented as a function of the hydrogen-to-metal ratio  $x$  for the simple hopping model (model 0) and for multiple site-blocking to the second (model 2) and third (model 3) neighbour.

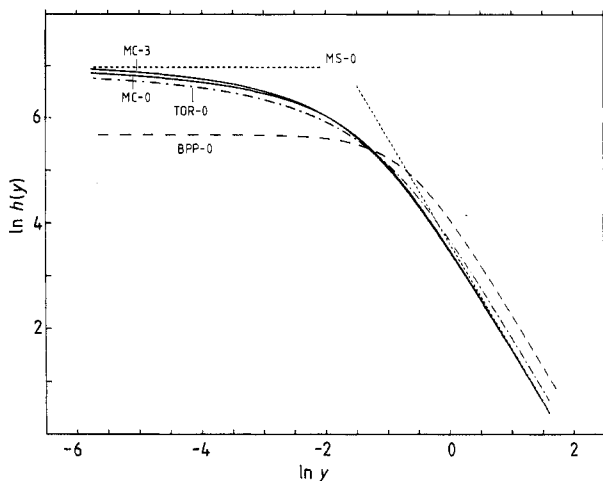
Model	$x$	$h(0)$	$C$	$A_1$	$A_2$	$A_3$
0	0.12	1070	266	0.067	-0.047	36.9
	0.3	1090	271	0.066	-0.030	37.1
	0.6	1110	281	0.066	0.004	37.6
2	0.12	1110	282	0.069	-0.030	37.2
	0.3	1180	313	0.069	0.038	38.3
	0.6	1330	377	0.067	0.222	41.3
3	0.12	1170	307	0.071	0.027	38.2
	0.3	1410	406	0.072	0.269	42.3
	0.6	2410	898	0.042	1.790	64.9



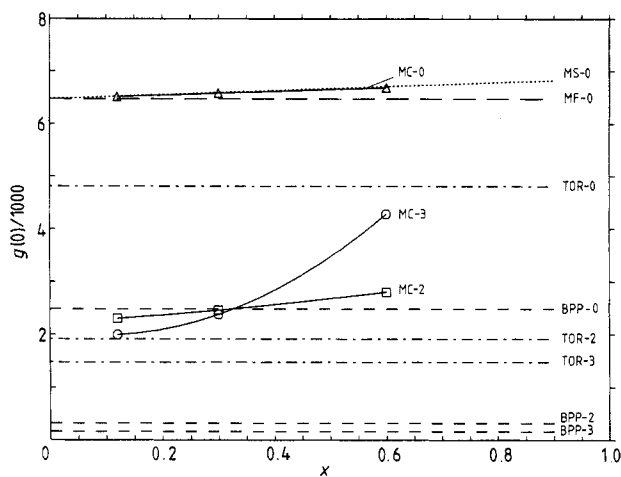
**Figure 1.** Plot of  $\ln g(y)$  versus  $\ln y$ . The MC results at  $x = 0.12$  are presented for the simple hopping model (labelled MC-0) and for blocking to the third neighbour (labelled MC-3). These are compared to the BPP, Torrey and MS theories for the simple hopping model.

MC results are in very satisfactory agreement with these limits. The Torrey and BPP models give poor agreement at low  $y$  but the agreement improves at larger values of  $y$ . The Torrey theory is an improvement over the BPP theory at all values of  $y$ . The MC results for blocking to the third neighbour may be compared to the results for the simple hopping model. The blocking model yields values for  $g(y)$  which are at least a factor of 3 smaller at low values of  $y$  and a factor  $>40$  smaller at larger values of  $y$  than the values for the simple hopping model. The value of  $g(y)$  drops because blocking is equivalent to weakening the hydrogen-hydrogen spin interaction. Multiple site-blocking does not affect the proximity to metal atoms, however, and so the value of  $h(y)$  is almost independent of the extent of the multiple site-blocking as shown in figure 2. The small difference which exists at low  $y$  is due to the slightly smaller tracer correlation factor





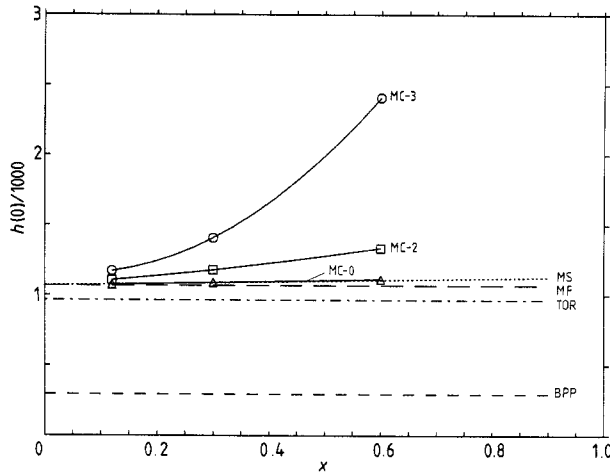
**Figure 2.** Plot of  $\ln h(y)$  versus  $\ln y$ . The MC results at  $x = 0.12$  are presented for the simple hopping model (labelled MC-0) and for blocking to the third neighbour (labelled MC-3). These are compared to the BPP, Torrey and MS theories for the simple hopping model.



**Figure 3.** Plot of  $g(0)$  versus  $x$ . The results from the MC, BPP, and Torrey theories are presented for the simple hopping model (0) and for the multiple site-blocking model with blocking to the second (2) and third (3) neighbour. The results of the MS and mean-field (MF) theories for the simple hopping model are also presented.

(and hence the tracer diffusion coefficient) at the concentration  $x = 0.12$  for the case where the blocking extends to the third neighbour. This difference would disappear, of course, in the limit  $x \rightarrow 0$ . Once again the agreement with the MS result in the small- and large- $y$  limit is very good.

In figures 3 and 4 we focus on the results for  $g(0)$  and  $h(0)$  and compare the values obtained as a function of concentration with those from the BPP, Torrey and MS theories. These quantities are important because they determine the small- $y$ , or high-temperature, limit of the relaxation rate and this is the region most accessible experimentally.



**Figure 4.** Plot of  $h(0)$  versus  $x$ . The results from the MC theory is presented for the simple hopping model (0) and for the multiple site-blocking model with blocking to the second (2) and third (3) neighbour. The results of the BPP, Torrey, MS and mean-field (MF) theories for the simple hopping model are also presented.

For instance, in the small- $y$  limit, the like-spin and unlike-spin relaxation rates are easily obtained from equations (2) and (3), namely,

$$T_{II}^{-1} = A\tau g(0) \tag{11}$$

$$T_{IS}^{-1} = 2B\tau h(0)/3 \tag{12}$$

The values of  $g(0)$  and  $h(0)$  predicted by the other theoretical models are also easily obtained. In the BPP model (see for example Zamir and Cotts 1964, Zogal and Cotts 1975),  $g(0)$  is equal to  $S_I$  and  $h(0)$  is equal to  $2S_S$ , where

$$S_I = G_I^*(0) = b^6 \sum_{i=1}^{\infty} r_i^{-6} \frac{P'(r_i)}{c} \tag{13}$$

$$S_S = G_S^*(0) = b^6 \sum_{m=1}^{\infty} r_m^{-6} \tag{14}$$

The summations are taken over values of  $r_i$  defined to be the distance from an occupied interstitial site to each surrounding interstitial site and for values of  $r_m$  equal to the distance from an occupied interstitial site to all metal sites. The BPP model predictions for  $g(0)$  and  $h(0)$  for the multiple site-blocking model may be obtained from equations (13) and (14) by using the approximation that  $P'(r_i)$  is zero when  $r_i$  corresponds to a site which is within the blocking distance, and equal to  $c$  elsewhere. The values of  $S_I$  and  $S_S$  obtained in this way are given in table 3.

The Torrey model is slightly more complicated and requires the evaluation of the functions  $G(k_H, 0)$  and  $G(k_M, 0)$  (using the notation of Resing and Torrey 1963), where

**Table 3.** The lattice summations  $S_I$  and  $S_S$  are given by equations (13) and (14) and the tracer correlation factor  $f$  is from Faux and Ross (1987). The remaining quantities are required in order to determine the spectral density functions using the Torrey model (see text).

Model	$S_I$	$S_S$	$f$			$k_H$	$k_M$	$G(k_H, 0)$	$G(k_M, 0)$
			$x = 0.12$	$x = 0.3$	$x = 0.6$				
0	2486.2	146.53	0.99	0.98	0.95	0.771	1.090	0.654	1.096
2	319.2	146.53	0.95	0.89	0.78	1.527	1.090	2.002	1.096
3	158.5	146.53	0.90	0.75	0.44	1.929	1.090	3.104	1.096

$k_H$  and  $k_M$  are lattice-dependent normalisation constants. The expressions for  $g(0)$  and  $h(0)$  using the Torrey model are,

$$g(0) = 3G(k_H, 0)S_I \quad (15)$$

$$h(0) = 6G(k_M, 0)S_S \quad (16)$$

The method of calculating these quantities is presented by Resing and Torrey (1963) and also by Weaver and VanDyke (1972). The relevant quantities are listed in table 3. Finally, the small- and large- $y$  limits of the MS model are presented by Sankey and Fedders in terms of the quantities  $b_0(0)$  and  $a_0(0)$  which are tabulated by the authors. In this case,  $g(0)$  is equal to  $b_0(0)$  and  $h(0) = 3a_0(0)/2$ .

The values obtained from each of these theories are plotted in figures 3 and 4. Only the MS and MC results depend on concentration and the agreement between the two for the simple hopping model is very satisfactory. Once again the Torrey model is an improvement over the BPP model for both  $g(0)$  and  $h(0)$ . Only the MC result, however, shows a sharp increase in the value of  $h(0)$  and  $g(0)$  with concentration for the case of blocking to the third neighbour. This effect arises because the hydrogen spins are forced to spend a greater amount of time in a small region of crystal due to the blocking effect of surrounding hydrogen spins.

We may use the results presented in figures 3 and 4 to compare with the experimental result of Zogal and Cotts (1975). These authors measured the tracer diffusion coefficient  $D$  and the  $T_1^{-1}$  relaxation rate for hydrogen in a sample of  $\text{NbH}_{0.6}$  and compared the quantity  $D/T_1$  with the predictions of the BPP theory (which they called the SRT, or single-relaxation-time theory) and the Torrey theory. Both gave poor agreement with the experimental result if it was assumed that the RMS jump length,  $\langle l^2 \rangle^{1/2}$ , equalled the nearest-neighbour distance. They were forced to conclude that  $\langle l^2 \rangle^{1/2}$  lay somewhere between  $0.5b$  and  $0.8b$  (between the second and fifth neighbour).

**Table 4.** The values of  $D/T_1$  for various models in units of  $10^{-9} \text{ m}^2 \text{ s}^{-2}$ .

Model	BPP	Torrey	MS	MC	Experiment
0	0.39	1.08	1.31	1.31	
2	0.21	0.74		1.03	$1.5 \pm 0.2$
3	0.11	0.40		1.03	

The predictions of the BPP, Torrey, MS and MC theories are compared to the experimental value of Zogal and Cotts in table 4. The values of  $D/T_1$  are obtained by multiplying equations (11) and (12) by the tracer diffusion coefficient  $D$ , equal to  $l^2 f/6\tau$ , and by substituting the values of  $h(0)$  and  $g(0)$  obtained from each theory. For the tracer correlation factor  $f$ , we use the result of Faux and Ross (1987) which is given in table 3. For the Nb/H system,  $\gamma_s/\gamma_I = 0.244$  and  $\gamma_I = 2.6752 \times 10^8 \text{ s}^{-1} \text{ T}^{-1}$ , and  $S$ , the spin quantum number of the niobium spins, is equal to  $\frac{9}{2}$ . The lattice parameter  $b$  is equal to  $3.42 \text{ \AA}$ ,  $Q$  is equal to 1 and  $l^2 = b^2/8$  for nearest-neighbour hops. The results are presented in table 4 and are slightly different from those published by Zogal and Cotts and by Sankey and Fedders because we have also included the tracer correlation factor  $f$  in these calculations. This factor was ignored by Zogal and Cotts and an approximate expression was used by Sankey and Fedders.

The results of the comparison are interesting. The agreement between the predictions of the MS theory and the MC method for the case of the simple hopping model is not surprising in view of the accuracy of the two techniques. These results are within the quoted experimental error, but fortuitously so, because the simple hopping model is inappropriate for the Nb/H system at high concentrations. The MS theory cannot be easily extended to the case of multiple site-blocking and so this comparison is confined to the BPP, Torrey and MC theories. Here the MC values are approximately  $\frac{2}{3}$  of the experimental value. The MC method gives similar results for both the second- and third-neighbour blocking models. This is because the smaller value of the tracer correlation factor for blocking to the third neighbour is compensated by larger values of  $g(0)$  and  $h(0)$ . The BPP model however is a factor 7 or 15 too low and the Torrey model is 2 or 4 too low for each of the multiple site-blocking models.

Following the same arguments as Zogal and Cotts, agreement between the MC result and experiment can be obtained if  $\langle l^2 \rangle^{1/2}$  lies between  $0.4b$  and  $0.45b$ . The jump distance is between the nearest neighbour ( $0.35b$ ) and the second nearest neighbour ( $0.5b$ ). Agreement with experiment can therefore be obtained if the spins make roughly equal combinations of nearest-neighbour and second-nearest-neighbour jumps. This is not unreasonable from a geometrical point of view as both the first- and second-neighbour sites are easily accessible whereas hops to more distance sites are most likely to occur via a first- or second-neighbour site. Of course a true comparison can only be made by evaluating the spectral density functions for a two-site hopping model.

#### 4. Conclusions

The Monte Carlo results presented in this paper demonstrate the effect of concentration and multiple site-blocking on the spectral density functions which determine the nuclear spin relaxation rates due to the translational diffusion of interstitial spins in BCC metals. Both the like-spin and unlike spin contributions are calculated. It is found that the BPP and Torrey models are generally in poor agreement with the MC data with the agreement worse at high concentrations and for greater blocking distances. The Torrey theory is, however, a significant improvement over the BPP theory and should prove adequate for systems with a low concentration of spins. Very good agreement is obtained with the MS theory in the high- and low-temperature limits presented by Sankey and Fedders. Comparison with the experimental data of Zogal and Cotts suggests that the hydrogen spins in Nb/H diffuse by a combination of nearest-neighbour and second-nearest-neighbour hops. This result is in contrast to Zogal and Cotts who, by comparison with

the Torrey and BPP theories, were forced to conclude that the RMS jump length was between the second and fifth neighbour.

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