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Nuclear quadrupolar relaxation in metal–hydrogen systems

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Abstract

The theory of nuclear spin relaxation of quadrupolar metal nuclei is considered for the ScH(D)$_x$ system for arbitrary values of concentration $c=x/2$ of the diffusing H(D). It is shown that the relaxation rates simply scale in magnitude as $c(1-c)$ and that the temperature dependence is independent of c.

Keywords: Metal; Hydrogen; Nuclear quadrupole relaxation

1. Introduction

Nuclear spin relaxation rates in metal–hydrogen systems often show anomalous behaviour at high hydrogen concentrations and high temperatures [1]. The anomalies are present in both metal hydrides and deuterides and occur for the relaxation of the fixed metal nuclei as well as for the relaxation of the diffusing hydrogen. In the case of ScH$_x$ and ScD$_x$ ($1<x<2$) the relaxation of ^{45}Sc is dominated by the quadrupolar interaction of the nucleus with the fluctuating electric field gradient (EFG) produced by diffusing protons or deuterons. The Sc dihydrides and dideuterides have a fluorite structure, with the metal lattice being fcc and the hydrogen diffusing between interstitial tetrahedral sites which form a simple cubic lattice.

A good understanding of the quadrupolar relaxation in the region away from the high-temperature anomalies is necessary in order to separate the anomalous features of the data. The usual expression for the quadrupolar relaxation rate [2] is only valid in the low concentration limit (atoms or vacancies) of sources of EFG. Since the ^{45}Sc relaxation data includes more general concentrations of hydrogen, it is of interest to determine the form of the relaxation behaviour for arbitrary hydrogen concentrations.

The theory of quadrupolar relaxation for arbitrary concentrations is more complicated than the corresponding theory of magnetic dipolar relaxation because three-particle correlations occur for the quadrupolar case which are negligible for the dipolar case [3]. The theory of relaxation of the diffusing species is therefore quite difficult [4]. The present case is for relaxation of a fixed nuclear species on a separate sub-lattice to the diffusing species. It is shown below that, in this case, a quite simple expression for the relaxation rate can be obtained.

2. Theory of quadrupolar relaxation

The model to be considered is of hydrogen randomly occupying the tetrahedral sites with an average probability c ($=x/2$ in ScH$_x$). The mean time τ between jumps of an atom is related to the mean time τ_a between attempted jumps by $\tau=\tau_a/(1-c)$. At any instant a metal nucleus at the centre of a cubic cell will experience an EFG due to a particular configuration of hydrogen surrounding it. It will be assumed that only nearest neighbours to the metal site contribute to the EFG and that the EFG due to hydrogen at a particular site arise from a central potential. The EFG components $V^{(q)}$ at a nucleus due to i occupied nearest neighbour sites are then [2]

$$V^{(q)} = eq_0 \sum_{\alpha=1}^{i} Y_{2q}(\Omega_\alpha), \tag{1}$$

where eq_0 is the EFG for axial symmetry, Y_{2q} is a spherical harmonic and Ω_α is the direction of a site α from the origin, relative to the direction of the applied magnetic field.

The relaxation rate is a linear combination of spectral density functions $J^{(q)}(\omega)$ which are the Fourier transforms of the correlation functions $G^{(q)}(t)$ of the EFG fluctuations. The correlation functions are

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$$G^{(q)}(t)=\overline{\langle V^{(q)}(0)V^{(q)*}(t)\rangle}. \tag{2}$$

The bar denotes an average over starting configurations of hydrogen at the nearest neighbour sites of a metal nucleus and an average over magnetic field directions appropriate to polycrystalline systems. The diagonal brackets denote an average over the time evolution of the system which corresponds to fluctuations between the possible configurations. Eq. (1) and Eq. (2) show that the correlation functions involve the product of two summations. It is the cross terms in this product that correspond to the three-particle correlation functions which occur in quadrupolar relaxation but which do not occur in dipolar relaxation.

An expression for $G^{(q)}(0)$ can be obtained by writing

$$G^{(q)}(0)=(eq_0)^2\sum_{i=1}^{7}p_i x_i \tag{3}$$

where $p_i=c^i(1-c)^{8-i}8!/[i!(8-i)!]$ is the probability of there being i atoms on the eight cubic sites around a metal nucleus and

$$x_i=\left\langle\sum_{\alpha,\beta=1}^{i}P_2(\cos\theta_{\alpha\beta})\right\rangle. \tag{4}$$

The average in Eq. (4) is over the possible arrangements of the i atoms on the eight sites. The indices α,β denote sites on the cube for the i atoms and $\theta_{\alpha\beta}$ is the angle between the direction from the centre of the cube to the α site and the corresponding direction to the β site. The Legendre polynomial $P_2(\cos\theta_{\alpha\beta})$ is unity if $\alpha=\beta$ or if α and β are diagonally opposite sites, and it is $-1/3$ otherwise. An expression for x_i can be obtained by noting that of the i^2 terms in the summations in Eq. (4), there are i terms which have $\alpha=\beta$ and $i(i-1)/7$ terms for which α and β are opposite along a cube diagonal; the contribution of each of these terms to the summation is unity. All other terms each contribute $-1/3$. Summing all of these then gives the result $x_i=i(8-i)/7$. The summation in Eq. (3) can then be evaluated analytically and the result is the simple expression $G^{(q)}(0)=8(eq_0)^2c(1-c)$ which shows the expected symmetry between c and $(1-c)$.

The time-dependence of $G^{(q)}(t)$ is needed to obtain the spectral density functions $J^{(q)}(\omega)$. In the low concentration limits $c\ll 1$ and $(1-c)\ll 1$ it is only necessary to consider the motion of a single atom or vacancy in evaluating $G^{(q)}(t)$. This motion can be described using random walk theory and the expression for the correlation function is obtained by considering the probabilities for diffusion from one neighbouring site of the metal atom to another in a time t. The expression for $G^{(q)}(t)$ is then

$$G^{(q)}(t)=8(eq_0)^2c[P(0,t)-P(\boldsymbol{l}_1,t)-P(\boldsymbol{l}_2,t)+P(\boldsymbol{l}_3,t)], \tag{5}$$

where $P(\boldsymbol{l}_j,t)$ is the probability of an atom (or vacancy) diffusing from the origin (a site on the simple cubic lattice adjacent to a metal nucleus) to a jth neighbour $\boldsymbol{l}_j$ in a time t. The coefficients of the $P(\boldsymbol{l}_j,t)$ in this expression are a result of the weighting of the number of such sites and the contribution to the correlation function from each. The functions $P(\boldsymbol{l}_j,t)$ can be evaluated numerically from the integral expression [5]

$$P(\boldsymbol{l},t)=\frac{1}{(2\pi)^3}\int_{-\pi}^{\pi}\int_{-\pi}^{\pi}\int_{-\pi}^{\pi}\cos(\boldsymbol{l}.\boldsymbol{\rho})e^{-t[1-A(\boldsymbol{\rho})]/\tau_a}\,d\rho_1\,d\rho_2\,d\rho_3\,, \tag{6}$$

where $A(\boldsymbol{\rho})=\frac{1}{3}(\cos\rho_1+\cos\rho_2+\cos\rho_3)$. The form of the normalised correlation function is shown in Fig. 1 which also shows the simple exponential form corresponding to the common BPP approximation.

The accuracy of the low concentration expression for other values of c was tested by comparing the random walk calculations with the results of Monte Carlo simulations to calculate $G^{(q)}(t)$ for arbitrary concentrations. The Monte Carlo results for $c=0.5$ are also shown in Fig. 1. The random walk approximation is remarkably accurate for all values of c. This suggests that the time scale of the decay of the correlation function is independent of c and is the attempt jump time τ_a rather than the actual jump time τ. This is quite different to dipolar relaxation, for which the actual jump time is the appropriate parameter [6]. This difference between dipolar and quadrupolar relaxation is a consequence of the presence of the cross terms in Eq. (2). For both relaxation mechanisms the site blocking effect slows the diffusion rate with increasing concentration of the diffusing species. An additional effect, however, for quadrupolar relaxation is that a jump of any of the nearest neighbour atoms of the metal site can cause a fluctuation in the correlation function. The number of such neighbours

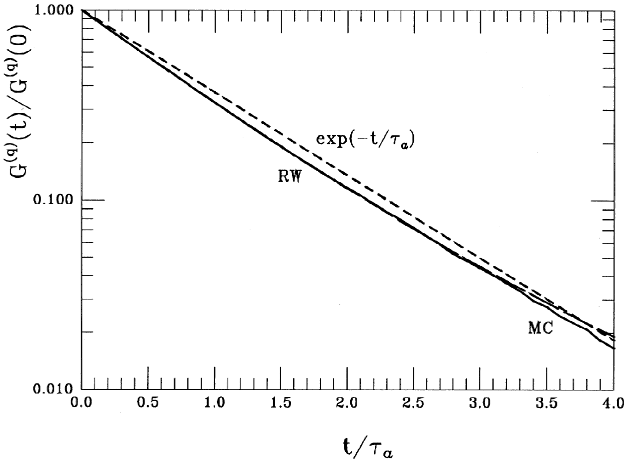

Fig. 1. The correlation function $G^{(q)}(t)/G^{(q)}(0)$ for the BPP model (short dashed curve), the low concentration limit random walk model (long dashed curve) and the Monte Carlo calculations (continuous curve) for $c=0.5$. The random walk and Monte Carlo results are indistinguishable on the scale of the graph for $t/\tau_a<3$.

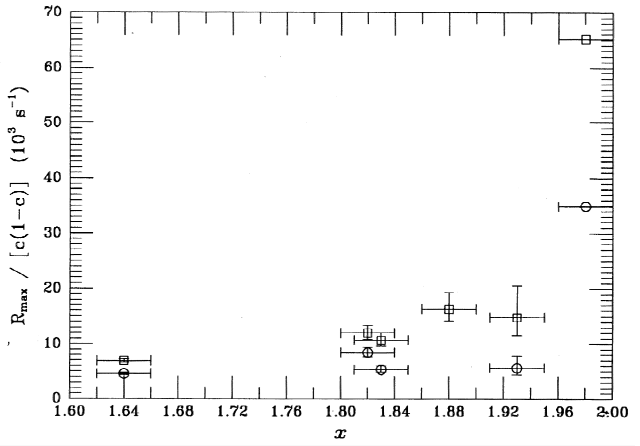

Fig. 2. Values of the maximum relaxation rate $R_{\mathrm{max}}/[c(1-c)]$ $(c=x/2)$ of ^{45}Sc in ScH$_x$ and ScD$_x$ at resonance frequencies 24 MHz (circles) and 12.2 MHz (squares). The error bars correspond to an uncertainty in x of ±0.02.

increases with concentration and this enhances the rate of decay of the correlation function, which compensates for the slower rate of diffusion.

The form of the correlation function $G^{(q)}(t)$, as a function of the atom concentration c, is therefore that its magnitude scales as $c(1-c)$ and that the time-dependence is independent of c and is the same as the low concentration limit. The resulting spectral density function $J^{(q)}(\omega)$ is therefore also proportional to $c(1-c)$ and is a function of $\omega\tau_{\mathrm{a}}$, which is independent of c. These results are also valid for the nuclear spin relaxation rates since they are linear combinations of spectral density functions.

3. Discussion

The implication of the above theory is that there is a universal curve for the relaxation rates of the metal nuclei as a function of temperature and concentration. At fixed frequency the magnitude of the relaxation scales with c as $c(1-c)$ for all temperatures and the position of the relaxation peak is independent of temperature. These conclusions for quadrupolar relaxation are different to those for dipolar relaxation [6].

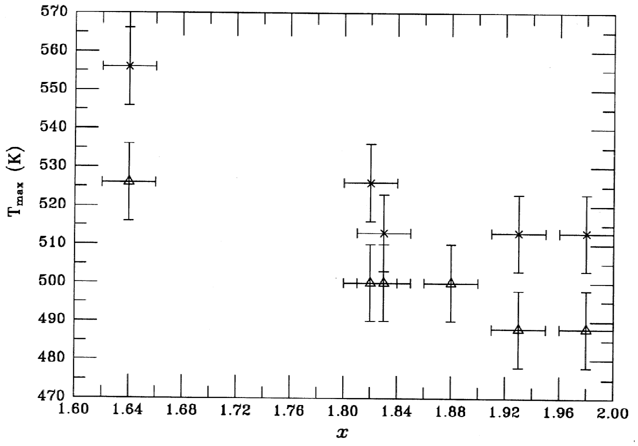

Fig. 3. Values of the temperature T_{max} at which the maximum relaxation rate occurs for the data in Fig. 2. The error bars for T_{max} correspond to ±10 K.

A comparison of these results with some spin-lattice relaxation data of ^{45}Sc in Sc hydrides and deuterides is shown in Fig. 2 and Fig. 3. The maximum relaxation rate R_{max}, scaled by the factor $c(1-c)$ $(c=x/2)$, is given as a function of the hydrogen concentration x in Fig. 2. The temperatures at which the maxima occur are shown for the same data in Fig. 3. The above theory predicts that both of these quantities would be independent of x. The data is only possible for a restricted range of concentrations because of phase changes. In addition, there may be complications because of the anomalous relaxation at high temperatures. The data in Fig. 2 are reasonably consistent with the above theory within the uncertainties involved, except at the highest x values. The data in Fig. 3 show a steady decrease in T_{max} values with increasing x at both resonance frequencies. Both the increase in $R_{\mathrm{max}}/[c(1-c)]$ at high x-values and the decreasing trend of T_{max} provide indications that hydrogen, although not occupying octahedral sites below 300 K, may be excited into such sites at higher temperatures on the order of T_{max}, as is known to occur in YH$_x$ for $x<2$ [7]. The fluorite structure hydrides of La and Zr may be able to show the theoretical effects described in Section 2 more clearly.

Acknowledgments

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