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Random Walk to and Interaction with an Impurity

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A random walker tagged with a spin may conveniently be studied by small amounts of paramagnetic impurities which significantly affect the spin relaxation at concentrations as low as a few parts per million. Examples are found in nuclear magnetic resonance (NMR) and muon spin rotation (μSR). At low temperature relaxation is determined by the time for the walker to reach an impurity, and thus the impurity acts like a simple trap. Details of the interaction with the impurity are important at higher temperatures, and the relaxation rate is shown to go through a maximum because of this. Special features associated with many returns to the origin, particularly important in one-dimensional walks, and the difference between incoherent (rapidly fluctuating paramagnetic spin) and coherent (stationary paramagnetic spin) returns are discussed.

KEY WORDS: Nuclear magnetic resonance; paramagnetic impurities; diffusion; low dimensionality.

1. INTRODUCTION

Small amounts of impurities or defects in a lattice can provide a useful probe of the random walk of a particle or excitation in the otherwise regular lattice. The most obvious example is that of an absorbing trap[1] into which the particle walks and cannot escape. The "lifetime" of the particle or its associated property being investigated is just the time required to execute a random walk from some starting point to a trap, suitably averaged over all random starting points and trap positions.

The impurity dealt with here is a paramagnetic ion in an otherwise nonmagnetic lattice which influences the spin relaxation of a diffusing particle. In some cases it acts like a simple trap so that the resulting spin

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relaxation time is the same as computed in trapping models. But in others, where the interaction is relatively weak and/or the particle motion fast, the situation is different: The spin is not completely relaxed in its encounter with the impurity and continues on to make other encounters. However, as opposed to a simple momentary trapping followed by escape picture, the particle's spin carries a memory of each previous encounter. Since the trapping model is treated in some detail elsewhere in this issue,[1] my main emphasis is on those aspects where the paramagnetic ion differs from a simple trap.

The experimental technique is most commonly nuclear magnetic resonance (NMR) which monitors the spin of the diffusing particle. Recently muon spin rotation (μSR) has also been employed[2] to study a diffusing particle, in this case the muon (μ-meson), by its interaction with impurities. Knowledge of how impurities affect the spin relaxation is important for two reasons. First, the impurity can prove to be a means of studying the diffusion. This is clearly illustrated by an example taken from μSR in Fig. 1. The muon maintains its spin polarization when brought to thermal equilibrium in a solid unless it interacts strongly with other spins. This can be accomplished by nuclear spins of the host in metals such as copper

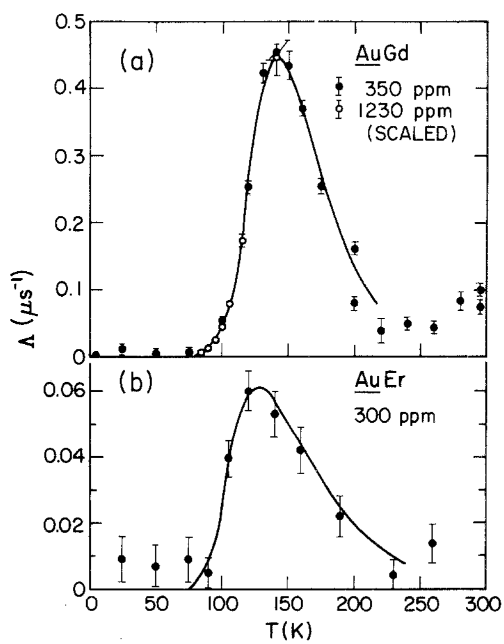

Fig. 1. Muon depolarization rates in gold doped with gadolinium and erbium, from Ref. 2.

which have strong nuclear moments, but not in silver and gold where the moments are very weak. Thus there is no convenient means of monitoring the muon in pure silver and gold but, as shown, a sizeable depolarization can be produced by small amounts of paramagnetic impurity. In this manner properties of muon motion in noble metals have been studied by the introduction of impurities.

A second reason is that the impurity question has to be dealt with whether one likes it or not. This is pointed out in Fig. 2 where one sees that as small as 20 parts per million (ppm) paramagnetic impurities make a sizable effect on the NMR. Nominally "pure" material generally has at least this high a concentration, so unless great care is taken, the NMR experimentalist will often be observing effects due to paramagnetic impurities, which obviously must be understood for meaningful interpretation of the results. Indeed it has become apparent with evidence such as in Fig. 2 that many earlier NMR phenomena which were either unexplained or proposed as evidence for exotic types of motion were in fact caused by unsuspected small amounts of paramagnetic ions.

The use of paramagnetic impurities to study particle motion in solids and their importance in understanding NMR was not fully appreciated

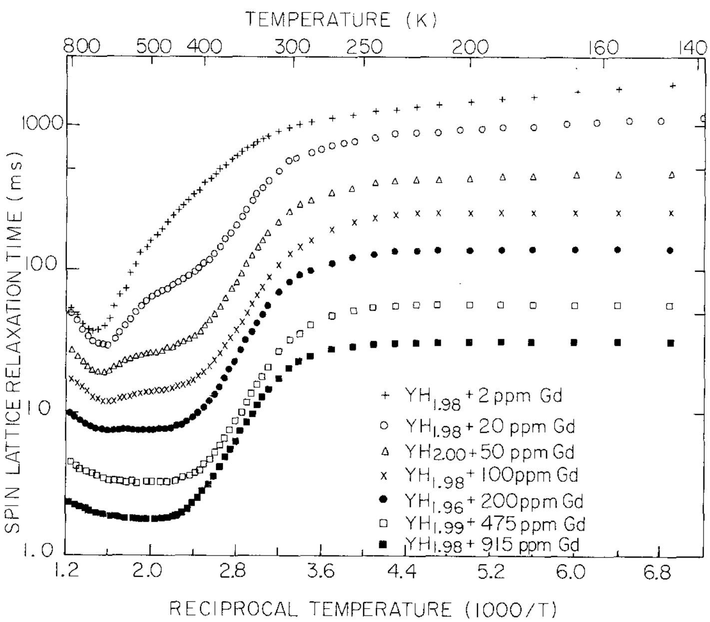

Fig. 2. Proton NMR relaxation in yttrium dihydride with various amounts of gadolinium impurities. Taken from M. Belhoul *et al.*, *J. Phys. F*, to be published.

Table I. Approximate Relations for Relaxation Rate T_R^{-1} and Conditions under which They Hold[a]

Type of walk	Type of returns	T_R^{-1} (traplike)	T_R^{-1} (weak interaction)
3D	incoherent, $\tau_{SL} \ll \tau$	$p\tau^{-1}, \Delta \gg 1$	$pA^2\langle S_z^2\rangle\tau_{SL}$
1D, $\langle x^2\rangle \propto t^{1-s}$	incoherent, $\tau_{SL} \ll \tau$	$p^{2/(1-s)}\tau^{-1}, \Delta \gg p^{(1+s)/(1-s)}$	$pA^2\langle S_z^2\rangle\tau_{SL}$
3D	coherent, $\tau_{SL} \gg T_R$	$p\tau^{-1}, \Delta \gg 1$	$pA^2\langle S_z^2\rangle\tau$
1D, $\langle x^2\rangle \propto t^{1-s}$	coherent, $\tau_{SL} \gg T_R$	$p^{2/(1-s)}\tau^{-1}, \Delta \gg p^{2(1+s)/(1-s)}$	$(pA^2\langle S_z^2\rangle\tau^2)^{2/(3+s)}\tau^{-1}$

[a] "Traplike" means spin is relaxed by first impurity it encounters, even though this impurity may be revisited many times for the 1D walk. "Weak interaction" means spin visits many different impurities before being relaxed. Conditions for this limit are the opposite ($\ll$ instead of $\gg$) of those for the traplike. $p \sim$ impurity concentration; τ_{SL} is the spin lattice relation time of the impurity ion; τ is the mean time between hops; $A^2\langle S_z^2\rangle$ is the mean square interaction frequency; and, $\Delta = A^2\langle S_z^2\rangle\tau\tau_c$, $\tau_c \approx \tau_{SL}, \tau$ for $\tau_{SL} \ll \tau$, $\tau_{SL} \gg \tau$, respectively.

until recent years[3] during which interest in diffusing nuclei has occurred in conjunction with active research on fast-ion (superionic) conductors and hydrogen in metals and metal hydrides. The pioneering work[3] of Jaccarino and co-workers at Santa Barbara has led to more thorough treatments,[4,5] to which the reader is referred for details. Numerous references to experimental work other than given here may be found in those references as well. The author has also dealt with how a one-dimensional (1D) random walk to an impurity gives rise to special effects.[6,7]

Since many of the details can be found elsewhere,[4–7] the present paper is meant to serve as a general introduction to the subject which emphasizes qualitative features. However, some new material related to walks with many returns to the same site, such as in 1D, is included with attention called to the differences between "coherent" and "incoherent" returns, depending on whether or not the spin of the paramagnetic ion fluctuates in the time from one return to the next. The results are summarized in Table I.

2. THEORY OF TEMPERATURE DEPENDENCE

It is evident from Fig. 1 and to a lesser extent from Fig. 2 that the relaxation rate due to paramagnetic impurities goes through a maximum vs. temperature. This feature is explained here where we point out that the two parts of the title "Walk to" and "Interaction with" can be identified with the low- and high-temperature sides of the peak, respectively.

The relaxation time T_R can crudely be considered as a sum

$$T_R = T_W + T_I \tag{1}$$

where T_W is the average "walk to" time it takes a particle to come to the neighborhood of an impurity and T_I is the additional time required for relaxation once the impurity is encountered. As long as the impurity does not affect the hopping rate in its vicinity, T_W is independent of the nature of the impurity and is the same as if the impurity were considered as an ideal trap. For normal thermally activated diffusion T_W is very long at low temperatures so that $T_R \approx T_W$ and traplike behavior is observed. As T_W decreases rapidly with temperature, it can become much less than T_I, in which case $T_R \approx T_I$ which depends on the nature of ("interaction with") the impurity. This is the situation of interest here, where the paramagnetic impurity gives results different from a simple trap. We show below that T_I is expected to be an increasing function of temperature which accounts for T_R going through a minimum.

The paramagnetic ion interacts with the nuclear or muon spin $\mathbf{I}$ by an effective field $\mathbf{H}_I$ which is proportional to components of the impurity spin

S. The generally complex problem can be simplified by assuming that $\mathbf{H}_I$ is only in the z direction of the applied field used to monitor the resonance and is proportional to S_z. Then the perturbation acts like a fluctuating frequency $\omega(t')$ which causes dephasing according to

$$I_+(t) = I_+(0)\exp\left[i\int_0^t \omega(t')\,dt'\right] \tag{2}$$

with $\omega(t') = A(t')S_z(t')$. I_+ is the observed rotating component of nuclear spin, and $A(t')$ is the interaction frequency whose time dependence is taken to be such that $A(t') = A$ for times the particle is at a nearest-neighbor distance from an impurity and zero otherwise. Time dependence of $S_z(t')$ comes from fluctuations with a characteristic spin lattice relaxation time τ_{SL} through coupling to lattice vibrations. (Coupling to other paramagnetic ions can also contribute to fluctuations, but we assume sufficiently low concentration that this can be ignored.) Treatments of more realistic interactions may be found in Refs. 4 and 5, but they do not differ qualitatively from what is presented here.

If the fluctuations of $S_z(t')$ are described by a Gaussian random process, Eq. (2) becomes, on the average over the states of $S_z(t')$,

$$\begin{aligned} I_+(\text{after})/I_+(\text{before}) &\equiv \phi(\tau) \\ &= \exp\left[-A^2\langle S_z^2\rangle\int_0^\tau (\tau - t')e^{-t'/\tau_{\mathrm{SL}}}\,dt'\right] \\ &\equiv e^{-\Delta} \end{aligned} \tag{3}$$

where τ is the time the particle remains at nearest-neighbor distance and "before" and "after" indicate times immediately before and after the encounter of duration τ. Note that if we define the correlation time τ_c by $\Delta = A^2\langle S_z^2\rangle\tau\tau_c$, then $\tau_c = \tau/2$, τ_{SL} in the respective limits $\tau \ll \tau_{\mathrm{SL}}$, $\tau \gg \tau_{\mathrm{SL}}$.

For $\Delta \gtrsim 1$, relaxation is essentially acheived in one encounter, which is the case for τ sufficiently long, i.e., low temperature. As τ and τ_{SL} shorten with increasing temperature, Δ becomes less than unity, and it takes more than one encounter to depolarize the spin. If each successive encounter is independent, the result of N_s encounters with impurities in time τ is to make the relaxation $\Phi(\tau) = [\phi(\tau)]^{N_s} = e^{-N_s\Delta}$. This is because there is no change in the amplitude of $I_+(t)$ during "free precession" time periods when no impurity is encountered. Thus the proper $I_+(\text{before})$ at the beginning of each encounter has an amplitude given by that of $I_+(\text{after})$ from the previous encounter. This is what is meant by the spin retaining a memory of each encounter—it can be relaxed in stages.

For $\Delta \ll 1$ it takes on the order of $1/\Delta$ encounters to achieve relaxation, which requires a time $T_I = T_W/\Delta$ since the average time between each encounter is T_W if the impurities are randomly located. Also if returns to the the same impurity are neglected, it follows that $T_W = \tau/p$, where p, proportional to the impurity concentration, is the probability that a given site on the walk is next to an impurity. Combining this with the definition of τ_c given under Eq. (3) yields

$$T_I \approx \left(pA^2\langle S_z^2\rangle\tau_c\right)^{-1} \qquad (\Delta \ll 1) \tag{4}$$

The noteworthy points are that the dwell time τ cancels out of the expression for T_I and that T_I is inversely proportional to a characteristic time τ_c whereas T_W is proportional to τ. Thus, T_W and T_I have opposite temperature dependences so that a minimum relaxation time $T_R = T_W + T_I$ is expected, as seen in Figs. 1 and 2. The dependence of T_I on the properties of the impurity is displayed in Eq. (4). As well as depending on the strength of the interaction, it depends on the spin lattice relaxation time $\tau_{\rm SL}$ if, as is often the case, $\tau_{\rm SL} \ll \tau$ so that $\tau_c \approx \tau_{\rm SL}$. This illustrates how spin relaxation by paramagnetic impurities can be used to advantage. At relatively low temperatures where $T_R \approx T_W$, properties of the random walk can be studied independent of the nature of the impurity, and at higher temperatures where $T_R \approx T_I$ one can study properties of the impurity and interactions.

3. FORMAL TREATMENT, MULTIRETURNS, AND COHERENCE

Having seen the qualitative features which produce a minimum relaxation time T_R vs. temperature, we proceed to a more formal development which reproduces the above results and also serves as a convenient means of treating walks with many returns to the origin, such as in 1D. Equation (2) is valid for all times within the framework of the model. For nearest-neighbor-only interactions we can write the integral as

$$\int_0^t \omega(t')\,dt' = A\sum_{i=1}^{N} p_i \sum_{k_i=1}^{n_i} \int_{t_{k_i}}^{t_{k_i}+\tau_{k_i}} S_i^z(t')\,dt' \tag{5}$$

where the first sum is over all *different* sites occupied by the particle during its walk, there being a total of N such sites in time t; $p_i = 1$ if the site i is a neighbor of impurity spin $\mathbf{S}_i$ and 0 otherwise. The ith site is visited a total of n_i times, the kth visit lasting between t_{k_i} and $t_{k_i} + \tau_{k_i}$. We assume that there is only one site i at which the particle can interact with $\mathbf{S}_i$. This is not the case for most real lattices, but it makes the analysis simpler without losing the essential features.

The observed relaxation is obtained by inserting Eq. (5) in (2) and performing an average over all the variables. The average over the impurity distribution p_i is handled in the same manner used in trapping studies.[1] For the other variables we consider two limits below.

3.1. Incoherent Returns

Assume the spin lattice relaxation is sufficiently rapid that $\tau_{\mathrm{SL}} \ll t_{k_{i+1}} - t_{k_i}$. In this case, each visit to the same site [each term in the summation over k_i in Eq. (5)] is independent since the spin S_z has lost all memory of its orientation at the previous visit. This "incoherent" condition is essentially the same as $\tau_{\mathrm{SL}} \ll \tau_{k_i}$ since the first return, if it occurs at all, is most probable on the next jump after the particle has jumped away from the origin. It then follows from Eq. (3) and the method of averaging over p_i that the total relaxation function is

$$\Phi(t) = \prod_{i=1}^{N} \left\langle \exp\left\{ -p\left[1 - \exp\left(-\sum_{k=1}^{n_i} \Delta_{k_i}\right)\right]\right\}\right\rangle \qquad (\tau_{\mathrm{SL}} \ll \tau_{k_i}) \qquad (6)$$

Δ_{k_i} is the same as Δ in Eq. (3) except that τ is replaced by τ_{k_i} to allow for a distribution of dwell times in general. For the ensuing discussion, however, we take $\tau_{k_i} = \tau$ and $\Delta_{k_i} = \Delta$, i.e., the same dwell time and relaxation at each encounter, in order to keep matters simple without altering the essential features. For $n_i\Delta \gg 1$, $\Phi(t) = \langle e^{-Np} \rangle$, which is the result for traps. In a 3D walk where $n_i \sim 1$ ($n_i \approx 1.5$, for example, for the average number of visits to a given site in a walk on a simple cubic lattice), this condition for trappinglike behavior is essentially just $\Delta \gg 1$, as in the previous section. In 1D, however, n_i increases without limit as a function of time so the situation is quite different. For the random walk of a single particle on a uniform 1D lattice, both n, the number of different sites visited, and n_i, the number of visits to the same site, are proportional to $(t/\tau)^{1/2}$. As a consequence the consistency condition for traplike behavior is that the relaxation time T_R satisfy $(T_R/\tau)^{1/2} p \approx 1$ while at the same time $(T_R/\tau)^{1/2}\Delta \gg 1$, i.e., $\Delta/p \gg 1$, which is much less stringent than the 3D condition $\Delta \gg 1$ when the concentration p is small. This result can be extended to some other models of 1D random walks[8,9] which are characterized by the mean square displacement satisfying $\langle x^2 \rangle \propto t^{1-s}$ with $0 < s < 1$, and thus $N \propto t^{(1-s)/2}$. A scaling argument[9] shows that $n_i \propto t^{(1+s)/2}$ and thereby produces the results shown in Table I.

The weak interaction limit is characterized by $\Delta n_i \ll 1$. In this case, the particle must visit several different sites in order to be relaxed, and Eq. (6) gives

$$\Phi(t) = \langle e^{-\Delta p \sum_{i=1}^{N} n_i} \rangle \qquad (\Delta n_i \ll 1,\ \tau_{\mathrm{SL}} \ll \tau) \qquad (7)$$

This has a simple interpretation since $\sum_{i=1}^{N} n_i$ is just the total number of hops, t/τ, in time t, which is independent of the geometry or other details of the walk. For example, from above, $Nn_i \propto t^{(1-s)/2} t^{(1+s)/2} = t$. Thus in this limit the relaxation rate always varies linearly with concentration for small p.

3.2. Coherent Returns

In the limit of very weak spin lattice relaxation the spin $\mathbf{S}_i$ maintains the same orientation for each visit to the site i. The returns are then said to be "coherent" and the coefficient of p_i in Eq. (5) reduces to $S_i^z(0)n_i\tau$, with $n_i\tau$ the total time spent at the site. As in Eq. (3) we approximate the average over the $2S+1$ possible values of $S_i^z = -S, -S+1, \ldots, S-1, S$ by a Gaussian so that

$$\Phi(t) \approx \prod_{i=1}^{N} \left\langle \exp\left\{ -p\left[1 - \exp(-\Delta n_i^2)\right]\right\}\right\rangle \tag{8}$$

where Δ is the same as in Eq. (3) with $\tau_{\mathrm{SL}} \to \infty$ and, as in the treatment following Eq. (6), we take $\Delta_{ki} = \Delta$, the same amount of relaxation for each visit. The product of averages in Eq. (8) is valid since the static orientations of $\mathbf{S}_i$ and $\mathbf{S}_j$ at different sites i and j are uncorrelated. Equation (8) differs from (6) only in that the factor n_i for incoherent returns is replaced by n_i^2 for coherent returns, which obviously can make a major change if $n_i \gg 1$.

It follows that the replacement of n_i by n_i^2 changes a result in Section 3.1 from $\Delta/p^r \gg 1$ to $\Delta/p^{2r} \gg 1$ as the condition for traplike behavior, where r is whatever exponent appeared in the expression for a given walk model. Thus, as expected, the trapping tendency (no need to find other impurities beyond the first) is greatly enhanced for coherent returns.

The weak interaction limit proves to be more interesting than in the incoherent case since the expression analogous to Eq. (7) would contain $\sum_{i=1}^{N} n_i^2 \sim Nn_i^2$, which *does* depend on details of the walk. From before, if $N \propto t^{(1-s)/2}$, $n_i \propto t^{(1+s)/2}$ for the 1D walk where $\langle x^2\rangle \propto t^{1-s}$, we have $Nn_i^2 \propto t^{(3+s)/2}$ whereby the concentration dependence of the relaxation rate is $T_R^{-1} \propto p^{2/(3+s)}$ compared with the simple linear dependence for incoherent returns.

4. DISCUSSION

We have given some qualitative and semiquantitative arguments for the dependence of relaxation time T_R due to paramagnetic impurities on temperature, concentration, and interaction strength. The results are summarized in Table I. Particular attention was paid to the question of when the impurity acts like a simple trap, in which case $T_R \approx T_W$, the time to walk to the impurity, and when it does not, in which case T_R is affected by details of the interaction and impurity spin lattice relaxation. The condition for $T_R \approx T_W$ was shown to be most easily satisfied for one-dimensional (1D) walks and coherent (very long spin lattice relaxation) returns.

Comparison between theory and experiment is disucssed in some detail in Refs. 2, 4, 5, and 7. The situation generally is that good agreement has been found in three-dimensional lattices when the calculation has been done in sufficient detail. Complications in this regard are that (i) the long-range r^{-3} part of the dipolar interactions, which has totally been neglected here, often has to be included. This makes a much more difficult problem which has mostly been handled by approximating the walk by a continuum diffusion,[10,11] although a discrete calculation has also been performed.[12] (ii) For most realistic 3D lattices the number of returns is significant so that a detailed lattice description is required. For example, if the particle hops on a simple cubic lattice with impurity sites at the body centers, there are an average of more than 4 visits to the 8 sites which are neighbors of an impurity, assuming one of these sites is visited initially. (iii) The interaction is not the simple form used here which includes only the z component of local field parallel to the applied field. Indeed, relaxation of the z component of nuclear spin, which is often what is observed rather than dephasing, is impossible in this case. A particularly thorough study which addresses (ii) and (iii) is contained in Ref. 5.

Several interesting features are predicted for 1D random walks to impurities. Although there are fast ion conductors which exhibit 1D motion, NMR studies[13] thus far have failed to give an unequivocal demonstration of the qualitative differences such as in concentration dependence. A major problem is that there is always some weak 2D or 3D character which may be sufficient to mask the effects unless the anisotropy of motion is extremely high. This point is treated in Ref. 7.

A challenge to the random-walk theorist can be to perform correctly the averages required in Eqs. (5) and (6) for arbitrary strengths of the interactions and values of the spin lattice relaxation. They have generally been done only in the extreme limits or with certain questionable asumptions regarding the processes.

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