Some quadrupolar effects on $T_1(H)$ for nuclear spins*

Peter A. Fedders
Department of Physics, Washington University, St. Louis, Missouri 63130
(Received 18 February 1976)

We calculate effects on $T_1(H)$ for nuclear spins due to several distinct interactions that depend on the quadrupole moment of the nuclear spins. We find, for example, that in metals the ratio $T_1(H\to\infty)/T_1(0)$ can be greater than 2 because of quadrupolar spin-spin interactions even in the absence of electric field gradients. We also show that $T_1(H)$ can depend on the spin I of a nucleus if T_1 is dominated by certain dynamic quadrupolar mechanisms.

I. INTRODUCTION

One of the predictions of single-spin-temperature theory is that T_1, the relaxation time of the spin temperature, has a characteristic dependence on the magnetic field H.[1] In metals where the nuclear spin Hamiltonian includes only a Zeeman term and a local-field term consisting of nuclear dipole plus exchange interactions, $T_1(H)$ should take the form

$$T_1(H)=T_1(H\to\infty)\,(H^2+h^2)/(H^2+2h^2), \tag{1}$$

where h is the local-field strength. This equation[1-3] is appropriate if the spin-lattice relaxation is due solely to the contact hyperfine interaction and there is no correlation between the relaxation of neighboring nuclear spins by the conduction electrons. According to Eq. (1), the ratio

$$R=T_1(H\to\infty)/T_1(H=0) \tag{2}$$

ought to be 2. However, this ratio has been measured in many metals both in the laboratory and rotating frames and the experimentally measured value of R always turns out to be greater than 2.[2-6] Effects due to static electric field gradients[1] or paramagnetic impurities can increase R, but in most of the above experiments these effects are believed to be negligibly small. The discrepancy is usually explained in terms of correlated relaxation via the conduction electrons,[4] although calculations of this effect are too small to explain it.[7]

Motivated by this persistent disagreement between theory and experiment, we have performed some simple calculations for $T_1(H)$ including a variety of interactions. Among other things, our calculations suggest a possible explanation for the discrepancy by showing that R can be greater than 2 because of quadrupolar spin-spin interactions alone without invoking electric field gradients or correlated decay. While we do not claim that this is the resolution of the discrepancy in all cases, we do believe that it is a likely candidate. Our procedure is to break the total spin Hamiltonian into a part $\mathcal{H}_0$ which depends only on the spin coordinates and $\mathcal{H}'$ which includes the spin-lattice interaction. In the rest of this section we will discuss the terms included in $\mathcal{H}_0$. In Sec. II we will discuss $\mathcal{H}'$, derive the results, and discuss them.

For the spin Hamiltonian (in the absence of spin-lattice interactions) we shall include terms linear in spin operators representing the interaction of a spin with spatially uniform and time-independent external fields. We also include terms bilinear in the spin operators at different sites representing the interaction between spins at different sites. In many ways the linear and bilinear terms are analogous to single-particle terms and interaction terms, respectively, in particle problems. The most general Hamiltonian that one can write under these conditions is

$$\mathcal{H}_0=\sum_l \mathcal{H}_l, \tag{3}$$

$$\mathcal{H}_l=-\sum \hbar\omega_{lm}A_{lm}(i) + \frac{1}{2}\sum \hbar\Omega^{(l)}_{m,m'}(i-j)A_{lm}(i)A_{lm'}(j), \tag{4}$$

where $A_{lm}(i)$ is the irreducible spin multipole operator[8] (l,m) at the site i, the first summation is over all sites i and all allowed m, and the second summation is over all lattice sites i and j with $j\neq i$ and over all allowed m and m'. The summation in Eq. (3) is over all integral values of l for $1\leq l\leq 2I$, where I refers to the nuclear spins in question. In writing the Hamiltonian in the form of Eqs. (3) and (4) we have broken with the traditional notation of magnetic resonance. This is necessary because traditional magnetic resonance notation cannot easily be generalized beyond the vector model.[8] Some advantages of the notation will become evident later in the paper. At present we wish to point out that a bilinear Hamiltonian cannot mix operators of different l.

We know of no case where terms other than the dipole ($l=1$) and quadrupole ($l=2$) terms in Eq. (3) are measurable and thus we shall concentrate on these terms. The first term on the right-hand side of Eq. (4) for $l=1$ is the Zeeman term and if the external magnetic field $\vec{H}$ is in the z direction, then $\omega_{1,0}=[\frac{1}{3}I(I+1)]^{1/2}\gamma H$ and $\omega_{1,1}=\omega_{1,-1}=0$, where γ is the spins' gyromagnetic moment. The second term on the right-hand side of Eq. (4) for $l=1$ includes all spin-spin interactions via the dipole or vector spin operators such as the dipolar and exchange terms. For $l=2$ the first term on the right-hand side of Eq. (4) is the "quadrupolar" term that describes the interaction of a spin with static electric field gradients. The second term on the right-hand side of Eq. (4) includes spin-spin interactions via the quadrupole spin operators. In fact the inclusion of this term is the only way in which our treatment differs from standard treatments up to this point.

Hamiltonians of the form in Eqs. (3) and (4) describe nuclear spin systems either in the lab frame or the rotating frame in the presence of an rf magnetic field strong enough for saturation.

II. CALCULATION

In this section we will calculate the magnetic field dependence of $T_1(H)$ due to two different spin-lattice relaxation mechanisms. The mechanisms considered are the interaction of the nuclear spins with an independent fluctuating dipole ($l=1$) field, such as the contact hyperfine interaction between the nuclear spins and conduction electrons, and an independent fluctuating quadrupole ($l=2$) field, such as the interaction of the nuclear spins with mobile hydrogen in metals or the usual spin-phonon interaction in certain regimes.

The field-dependent part of $T_1(H)$ can be calculated by the formula[1,2]

$$1/T_1(H)=-C\,\mathrm{Tr}[\mathcal{H}_0,\mathcal{H}']^2/\mathrm{Tr}\,\mathcal{H}_0^2, \tag{5}$$

where $\mathcal{H}_0$ is the spin Hamiltonian in the absence of spin-lattice interactions, $\mathcal{H}'$ is the spin-lattice Hamiltonian, and C is a constant. The quantity $\mathrm{Tr}\,\mathcal{H}_0^2$, which must be calculated for either spin-lattice mechanism, is easily obtained using the properties of the multipole operators

$$(A_{lm})^\dagger=(-1)^m A_{l,-m}, \tag{6a}$$

$$\mathrm{Tr}\,A_{lm}(A_{l'm'})^\dagger=(2I+1)\,\delta_{ll'}\delta_{mm'}. \tag{6b}$$

The calculation is a trivial extension of earlier calculations[1] and yields

$$\mathrm{Tr}\,\mathcal{H}_0^2=N(2I+1)^N\hbar^2\sum_l(|\omega_l|^2+|\Omega_l|^2), \tag{7}$$

where N is the number of nuclear spins and we have introduced the short-hand notation

$$|\omega_l|^2=\sum_m|\omega_{lm}|^2, \tag{8a}$$

$$|\Omega_l|^2=\frac{1}{2}\sum_{m,m',i}|\Omega^{(l)}_{mm'}(i)|^2. \tag{8b}$$

Thus $\mathrm{Tr}\,\mathcal{H}_0^2$ is a sum of single-particle terms $|\omega_l|^2$ and interaction terms $|\Omega_l|^2$ for each l.

The first spin-lattice mechanism which we consider is one in which the nuclear spins interact with some independently fluctuating dipole field which is spherically symmetric. The prime example of this, of course, is the interaction of the nuclear spins with the conduction electrons in a metal.[1,2] The Hamiltonian for this interaction can be written as

$$\mathcal{H}'=-\sum_i\{I_z(i)\,\beta_z(i)+[I_+(i)\,\beta_-(i)+I_-(i)\,\beta_+(i)]/\sqrt{2}\}, \tag{9}$$

where $(\beta_m)^\dagger=\beta_m$ describes the vector or dipole ($l=1$) independently fluctuating field. Although correlations can be included, here we shall make the simplifying assumption that the fluctuations at different sites are uncorrelated and thus

$$\mathrm{Tr}\beta_m(i)\,\beta^\dagger_{m'}(j)=A^2\,\delta_{m,m'}\delta_{i,j}. \tag{10}$$

In this case, using the commutation relations

$$[I_z,A_{lm}]=mA_{lm}, \tag{11a}$$

$$[I_\pm,A_{lm}]=[l(l+1)-m(m\pm1)]^{1/2}A_{lm\pm1}, \tag{11b}$$

along with Eqs. (6), one easily obtains

$$\mathrm{Tr}[\mathcal{H}_0,\mathcal{H}']^2=-N(2I+1)^N A^2\hbar^2\times\sum_l l(l+1)(|\omega_l|^2+2|\Omega_l|^2). \tag{12}$$

Thus, $T_1(H)$ can be written as

$$\frac{T_1(H)}{T_1}=\frac{2\sum_l(|\omega_l|^2+|\Omega_l|^2)}{\sum_l l(l+1)(|\omega_l|^2+2|\Omega_l|^2)}. \tag{13}$$

If only $l=1$ and $l=2$ terms are included, this reduces to

$$\frac{T_1(H)}{T_1}=\frac{|\omega_1|^2+|\Omega_1|^2+|\omega_2|^2+|\Omega_2|^2}{|\omega_1|^2+2|\Omega_2|^2+3|\omega_2|^2+6|\Omega_2|^2}. \tag{14}$$

Further discussion of this equation will be deferred to later in this section.

The other spin-lattice relaxation mechanism that we wish to consider is the interaction of the nuclear spins with some independently fluctuating quadrupole ($l=2$) field which can be described by the Hamiltonian

$$\mathcal{H}'=-\sum_{m,i}A_{2,m}(i)\,\beta^\dagger_{2,m}(i), \tag{15}$$

where $\beta^\dagger_{2,m}=(-1)^m\beta_{2,-m}$ describes the fluctuating

quadrupole field. Spin-lattice relaxation via this mechanism has recently been considered in some detail,[9] and it can refer to a variety of situations. For example, this mechanism describes first-order Raman and anharmonic Raman spin-lattice relaxation processes.[10] Another example is the relaxation of nuclear spins by mobile charged impurities such as hydrogen[9] or conduction electrons.[11]

The calculation of $\mathrm{Tr}\,[\mathcal{H}_0,\mathcal{H}']^2$ for this mechanism is perfectly straightforward but somewhat tedious. Since the calculation is almost identical to parts of the calculation in Ref. 9, it will not be repeated here. The results are almost unmanageable unless one makes the assumption that the quadrupole fluctuations are spherically symmetric and independent at different sites, i.e.,

$$\mathrm{Tr}\beta_m(i)\,\beta^{\dagger}_{m'}(j)=A^2\,\delta_{m,m'}\,\delta_{i,j}. \tag{16}$$

With these assumptions, one obtains

$$\mathrm{Tr}\,[\mathcal{H}_0,\mathcal{H}']^2=-N(2N+1)^N\hbar^2A^2\,[30/I(I+1)]\times\sum_l \alpha(l)\,(|\omega_l|^2+2|l_l|^2). \tag{17}$$

We have calculated $\alpha(l)$ only for $l=1,2$ and obtain

$$\alpha(1)=1,\qquad \alpha(2)=3(4I^2+4I-7)/(4I^2+4I-3). \tag{18}$$

Thus, including only $l=1$ and $l=2$ terms, we obtain

$$\frac{T_1(H)}{T_1}=\frac{|\omega_1|^2+|\Omega_1|^2+|\omega_2|^2+|\Omega_2|^2}{|\omega_1|^2+2|\Omega_1|^2+\alpha(2)\,(|\omega_2|^2+2|\Omega_2|^2)}. \tag{19}$$

The quantity $\alpha(2)$ increases monotonically as I increases with $\alpha(2)=0.6$ for $I=1$ and $\alpha(2)=3$ as I approaches infinity. Thus for nuclei with large spin, Eqs. (14) and (19) are identical. The case of $I=1$ is unique in that it is the only case in which $\alpha(2)$ is less than 1. Thus in the case where $|\omega_2|$ dominates $|\Omega_1|$ and $|\Omega_2|$, the ratio $R=T_1(\infty)/T_1(0)$ is just $\alpha(2)$ which could be less than 1 assuming that a single-spin temperature obtains under these conditions.

Probably the most striking part of these results is effect of the inclusion of quadrupole ($l=2$) spin-spin interactions on $T_1(H)$ for metals. In the absence of paramagnetic impurities and electric field gradients, one obtains a ratio R of

$$R=(2|\Omega_1|^2+6|\Omega_2|^2)/(|\Omega_1|^2+|\Omega_2|^2). \tag{20}$$

Thus R can be greater than two without invoking correlations among the conduction electrons or static electric field gradients. Unfortunately, estimates of the magnitude of $|\Omega_2|^2$ are not easy to obtain. Certainly indirect quadrupole spin-spin interactions do exist in metals by mechanisms similar to those that lead to indirect dipolar or exchange nuclear interactions via the conduction electrons. However, even the magnitude of these pseudodipolar ($l=1$) interactions are difficult to calculate and the pseudoquadrupolar ($l=2$) strengths are certainly no easier. Mitchell[11] has made crude estimates of the quadrupolar spin–conduction-electron interaction and found that it can be comparable with the dipolar spin–conduction-electron interaction for nuclei with large quadrupole moments. Estimates of the ratio of the pseudoquadrupolar interaction to the pseudodipolar or exchange interactions give comparable ratios. Trying to deduce the magnitude of $|\Omega_2|^2$ from line-shape or moment measurements is also very hard. The isotropic part of the pseudoquadrupolar spin-spin interaction would be very difficult to separate from the pseudoexchange spin-spin interaction. Neither contributes to the second line-shape moment and both contribute isotropically to the fourth line-shape moment.

On the other hand, one does not need a very big factor of $|\Omega_2/\Omega_1|^2$ in order to explain an appreciable observed shift of R from 2. For example, the value of $R=2.15$ appropriate[5,6] for pure Na can be explained by a factor of $|\Omega_2/\Omega_1|^2=0.039$. Even for the relatively large value of $R=2.58$ for pure Al,[4] one needs only a factor of $|\Omega_2/\Omega_1|=0.17$. Perhaps one of the best candidates for observing the effect would be Ta which has a very large quadrupole moment and thus should have a relatively large quadrupole spin-spin coupling.

ACKNOWLEDGMENT

The author would like to thank Professor R. E. Norberg for stimulating discussions and for comments on the manuscript.

*Supported in part by the National Science Foundation.

[1]See, for example, L. C. Hebel, Solid State Phys. 15, 409 (1963).

[2]L. C. Hebel and C. Slichter, Phys. Rev. 113, 1504 (1959).

[3]A. G. Redfield, IBM J. Res. Dev. 1, 19 (1957).

[4]A. G. Anderson and A. G. Redfield, Phys. Rev. 116, 583 (1959).

[5]D. Jerome and M. Galleron, J. Phys. Chem. Solids 24, 1557 (1963).

[6]J. Portrenaud, thesis (CNRS No. 242, Paris, 1966) (unpublished).

[7]P. A. Wolff, Phys. Rev. 129, 84 (1963).

[8]The use of the irreducible spin multipole operators is

rare in magnetic resonance although not so rare in other branches of physics. For a brief description of their use in magnetic resonance see P. A. Fedders [Phys. Rev. B 11, 995 (1975)].

[9]Peter A. Fedders, Phys. Rev. B 10, 4510 (1974).
[10]J. Van Kranendonk and M. B. Walker, Can. J. Phys. 26, 2441 (1968).
[11]A. H. Michell, J. Chem. Phys. 26, 1714 (1957).