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DISCLAIMER

NUCLEAR SPIN RELAXATION RATES BY NMR ON ORIENTED NUCLEI; Co^{60}$\underline{Co}$.

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ABSTRACT

We have applied a general multipole relaxation theory recently

developed by one of the authors to the interpretation of the nuclear

spin-lattice relaxation times of Co^{60} in Co at nuclear orientation

temperatures.   In order to do this a numerical method for calcul-

ating the relaxation factors for high spins at low temperatures

was developed.   The initial conditions and experimental details

are discussed.

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1. INTRODUCTION.

The measurement of nuclear spin-lattice relaxation times, T_1, is essential

to an understanding of heat transfer from nuclei to electrons or lattice.

The mechanisms of this energy change are basic to hyperfine interactions

and a knowledge of them can add to our understanding of these interactions.

One of the most fruitful techniques for observing such relaxation is nuc-

lear magnetic resonance (NMR). Several static or dynamic methods have

evolved so far. These include studies of saturation in continuous wave

experiments [1], decay after saturation by a pulse or series of pulses [2],

and others such as decay after adiabatic passage [3]. These earlier

methods are all based on observation of nuclear magnetization and have

usually been limited to temperatures above 1°K although the development

of the dilution refrigerator will probably extend the limit to ~ .05°K.

In addition, the samples are restricted to relatively large numbers of

nuclei (10^{20}) which makes the study of very dilute alloys impossible.

These two limitations on T_1 measurement were reduced when Templeton and

Shirley [4] illustrated measurement of T_1 by NMR on oriented nuclei

(NMR/ON). Here the resonance of oriented radioactive nuclei is detected

by observing the resulting perturbation of the γ-ray anisotropy. With

this method spin-lattice relaxation can be studied in very dilute alloys

in the temperature region 0.1 - 0.004°K.

However, the interpretation of the observed signal in NMR/ON is complicated

because one observes a nuclear radiation pattern whose directional intensity

is described by k^{th} rank statistical tensors, B_k.   Shirley [5] presented

the first explanation of these complications which was followed by the low-

temperature results on Co^{60} in Fe [6].   Other authors [7,8] have extended

the theory.   Gabriel [9] has developed a theory describing the relaxation

of these tensors in terms of a unique T_1 defined exactly as in previous NMR

work.   He also has given guide lines for calculating his relaxation factors,

$G_{k\ k'}^{q\ q'}$ (t), at low temperatures.   The aim of this paper is to present the

analytical solution for I = 1 and a numerical method for obtaining $G_{k\ k'}^{o\ o}$ (t)

for any spin at nuclear orientation temperatures.   In addition, the initial

conditions are discussed and the theory is applied to the relaxation of Co^{60}

in Co down to .006°K.

2.   THEORY.

2.1.   General.

The theoretical basis for the present paper has been laid in Gabriel's

paper [9] (hereafter called I) and we recall only a few formulae with-

out going through the details of their derivation.   Measurement of

nuclear spin-lattice relaxation times by radiative detection methods

is but one example that can be interpreted in terms of the more general

theory of multipole relaxation.   For a system with axial symmetry the

angular distribution perturbed by the presence of relaxation effects
can be written as:-

$$W_{axial} (\underset{\sim}{k};t) \equiv W(\theta;t) = \sum_{k} U_k F_k P_k (\cos \theta) B_k(t), \qquad (1)$$

Where the $U_k F_k$ depend on the decay scheme, $P_k (\cos \theta)$ is a Legendre
polynomial, and the $B_k(t)$ are time-dependent orientation parameters.
The latter can be given the form (see EQN I.100)

$$\Delta B_k(t) = B_k(t) - B_k(eq) = \sum_{k'} G_{k\ k'}^{o\ o}(t) \; \Delta B_{k'} \; (t = 0) \qquad (2)$$

$$= \sum_{k'} (U_o^k | \exp \left\{ -(iL' + \bar{M})t \right\} | U_o^{k'}) \; \Delta B_{k'}(t = 0).$$

The perturbation factors $G_{k\ k'}^{o\ o}(t)$ (the same as used in perturbed
angular correlation theory) are the matrix elements of an evolution
operation with respect to Fano's multipole representation.   The
Liouville operator L' describes all static extranuclear interactions,
whereas the relaxation operator $\bar{M}$ contains the properties of the
surroundings into which the nuclei are embedded.   In the present
paper, we consider only magnetic relaxation processes with static
magnetic fields.   The extension to axially symmetric field
gradients with the same axis as the magnetic field is straight for-
ward (further generalization to asymmetric cases just increases the
numerical calculation considerably).

Equation 2 shows that the orientation parameters depend on the properties of the environment(a contribution which is independent of the special type of experiment under consideration) and the preparation of the initial state. We will see in the following that the magnitude of the spin-lattice relaxation time is rather sensitive to changes in the initial conditions.

As mentioned in I, Section VI, we can either diagonalize the matrix in the exponential of (2) or invert a finite-dimensional matrix in Liouville space in order to calculate the resolvent (the Laplace or Fourier transforms of the time dependent exponential)

$$G \, _{k \, k'}^{q \, q} \, (p) \;=\; \left(U_q^k \, \Big| \, \left[p \cdot \hat{E} + iL' + \bar{M} \right]^{-1} \Big| \, U_q^{k'} \right). \tag{3}$$

According to the assumed cylindrical symmetry of the system terms with different multipole orientation q do not mix and the dimension of the matrices involved in (2) or (3) reduce to (k x k). The multipole order k of the normalized multipole operators is related to the nuclear spin by $0 \le k \le 2I$.

The only matrix elements of the static Liouville operator, $L' = L_{magn} + L_{quad}$, (defined by Eqns. I 52-53) that are needed for the calculation of $G \, _{k \, k'}^{o \, o}$ vanish, since the structure constants $c \, _{o \, o \, o}^{K \, k' \, k} = 0$. (See the appendix in I for the

quantities c $\begin{pmatrix} K & k' & k \\ Q & q' & q \end{pmatrix}$).   The influence of an axially symmetric

quadrupole interaction is therefore restricted to slight changes

of the relaxation matrix and possible modifications of the system's

preparation due to the asymmetric level splitting.   These arguments

fail if the symmetry axis of the field gradient does not coincide

with the directions of the magnetic field.

The following tridiagonal matrix has to be inverted in order to get

$G_{k\,k'}^{0\,0}$ (t) (k, k' = 1, 2 .....2I).

$$
\left(G_{k\,k'}^{0\,0}(p) \right) = \begin{bmatrix} p+\lambda_{10} & \bar{M}_{12}^{00} & 0 & 0 & --- \\ \bar{M}_{21}^{00} & p+\lambda_{20} & \bar{M}_{23}^{00} & 0 & --- \\ 0 & \bar{M}_{32}^{00} & p+\lambda_{30} & \bar{M}_{34}^{00} & --- \\ | & - & - & - & ----------- \end{bmatrix} \tag{4}
$$

As in I, we have set:-

$$
\lambda_{ko} \equiv \left(U_0^k \,|\, \bar{M} \,|\, U_0^k \right) = k\,(k+1)\,/\,2T_1 \tag{5a}
$$

$$
\bar{M}_{k\,k\pm1}^{0\,0} \equiv \left(U_0^k \,|\, \bar{M} \,|\, U_0^{k\pm1} \right) \tag{5b}
$$

which have the following closed forms:-

$$\left(U_o^k \mid \bar{M} \mid U_o^{k+1}\right) = -\frac{1}{T_1} \tanh (x) \; k(k+1) \left\{\frac{(k+1) \; (k+2I+2) \; (2I-k)}{(2) \; (2k+1) \; (2k+2) \; (2k+3)}\right\}^{\frac{1}{2}} \quad (5c)$$

$$\left(U_o^k \mid \bar{M} \mid U_o^{k-1}\right) = \frac{1}{2T_1} \tanh (x) \; k(k+1) \left\{\frac{(k+2I+1) \; (2I-k+1)}{(2k+1) \; (2k-1)}\right\}^{\frac{1}{2}} \quad (5d)$$

with $x = \hbar\omega/2kT$.

The relaxation matrix is thereby expressed in terms of the longitudinal spin-lattice relaxation time, T_1, defined in exactly the same way as in ordinary NMR.

2.2 <u>Analytical Solution for I = 1.</u>

For I = 1 we find explicitly

$$\bar{M}_{12}^{oo} = -\frac{1}{\sqrt{3}} \left(\frac{\sigma}{T_1}\right) \quad ; \quad \bar{M}_{21}^{oo} = \sqrt{3} \left(\frac{\sigma}{T_1}\right)$$

$$\lambda_{10} = \frac{1}{T_1} \quad \quad ; \quad \lambda_{20} = \frac{3}{T_1}$$

with $\sigma = \tanh(x)$. The Laplace transform of the perturbation factors, $G_{k\ k'}^{o\ o}(p)$ is given by

$$
\begin{pmatrix} G_{11}^{oo}\ (p) & G_{12}^{oo}\ (p) \\ \\ G_{21}^{oo}\ (p) & G_{22}^{oo}\ (p) \end{pmatrix} = \frac{1}{\Delta} \begin{pmatrix} p+\lambda_{20} & -\bar{M}_{12}^{oo} \\ \\ -\bar{M}_{21}^{oo} & p+\lambda_{10} \end{pmatrix} \tag{6a}
$$

with

$$
\Delta = (p + \lambda_{10})\ (p + \lambda_{20}) + \bar{M}_{12}^{oo}\ \bar{M}_{21}^{oo}. \tag{6b}
$$

Except for the case that (6b) has a double root, the following time-differential perturbation factors emerge from (6a):-

$$
G_{12}^{oo}\ (t) = \frac{1}{2\sqrt{3}}\ \sinh\ (x)\ \left[e^{-\beta t} - e^{-\alpha t} \right]
$$

$$
G_{21}^{oo}\ (t) = \frac{\sqrt{3}}{2}\ \sinh\ (x)\ \left[e^{-\alpha t} - e^{-\beta t} \right]
$$

$$
G_{11}^{oo}\ (t) = \frac{1}{2} \left(1-\cosh(x) \right) e^{-\alpha t} + \frac{1}{2} \left(1+\cosh(x) \right) e^{-\beta t} \tag{7}
$$

$$
G_{22}^{oo}\ (t) = \frac{1}{2} \left(1+\cosh(x) \right) e^{-\alpha t} + \frac{1}{2} \left(1-\cosh\ (x) \right) e^{-\beta t}
$$

with

$$
x = \hbar\omega/2kT\ ;\ \alpha = \left[2+(\cosh\ x)^{-1} \right] / T_1\ ;\ \beta = \left[2-(\cosh\ x)^{-1} \right]/T_1.
$$

The off-diagonal perturbation factors go to zero with increasing temperature whereas the high-temperature solution (I.102) is restored by G_{11}^{oo} (HT) $\approx$ exp $(-t/T_1)$ and G_{22}^{oo} (HT) $\approx$ exp $\left(\frac{-3t}{T_1}\right)$.

2.3 Numerical solution for I = 5.

Even with the assumptions of the present paper, the matrix elements, $(U_o^k \mid$ exp $(-\bar{M}t) \mid U_o^{k'})$, are nondiagonal in the low-temperature regime. Therefore, diagonalization of the relaxation operator is required yielding (under certain conditions) a complete set of eigenvectors, $\mid \varkappa)$ belonging to the eigenvalues $\Lambda_\varkappa$. Eq. (2) (with $L' = 0$) can be given the form

$$\Delta B_k(t) = \sum_{k'\varkappa} (U_o^k \mid \varkappa)e^{-\Lambda_\varkappa t}(\varkappa \mid U_o^{k'}) \Delta B_{k'}, (t = 0) \qquad (8)$$

where the transformation matrix $a_{k\varkappa} \equiv (\varkappa \mid U_o^k)$ obeys the relations

$$\sum_\varkappa a_{k\varkappa} a_{k'\varkappa}^* = \delta_{kk'}. \qquad (9)$$

In the numerical calculations the initial conditions have been used to normalize the eigenvectors in an appropriate way. In the I = 1 case the transformation matrix elements can be taken explicitly from Eqns. (7) as functions of the Larmor frequency ω, the temperature, T, and the relaxation time T_1. For higher spins Eq.(5) must be used,

The various perturbation factors $G_{kk'}^{oo}(t)$ are easily obtained from Eq. (8) by choosing a set of special initial conditions: $\Delta B_{k'= \alpha}$ $(t=0) = 1$, $\Delta B_{k' \neq \alpha}(t=0) = 0$ for all possible choices of $\alpha = 1,2,..2I$. The result can be cast into the form

$$G_{kk'}^{oo}(t) = \sum_{\varkappa} (U_o^k | \varkappa)(\varkappa | U_o^{k'}) \, e^{-\Lambda_\varkappa t} \qquad (10)$$

$$- \sum_{\varkappa} A_{kk'}^{\varkappa} \, e^{-\Lambda_\varkappa t} \quad (k,k' = 1,2,\ldots(2I)).$$

Numerically, $G_{kk'}^{oo}(t)$ will be a function of x and must be evaluated for each x. The method finds application in its ease of extension to higher spins.

As an example we have chosen $I = 5$ at $x = 0.3$. In Figure 1 we present $G_{1k'}^{oo}$, $G_{2k'}^{oo}$, and $G_{4k'}^{oo}$ as a function of t/T_1. At $x = 0.3$ it is not necessary to consider k values above $k = 4$ because B_k for $k > 4$ are approximately zero as seen in Figure 2 which gives B_k as a function of x for $I = 5$.

2.4. Variation of Initial Conditions.

As one can see in equation (8) $\Delta B_k(t)$ for a given spin can be expressed as a sum of exponentials with arguments dependent only on the temperature and time and amplitudes dependent on the temperature and initial conditions. This emphasizes the dependence of the accuracy of T_1 measurements on correct knowledge of the initial conditions. In order to illustrate the sensistivity of $\Delta B_k(t)$ to

the initial conditions we have treated three cases for $I = 5$ at x
(equilibrium) = 0.3 (corresponds to $10m°K$ for Co^{60} in Co fcc) which
are shown in Figure 3.   The first case is x (initial) = -0.3 which
inverts B_k with k odd and does not change B_k with k even (this
corresponds to a negative temperature).   The qualitative shape of
the recovery of B_1 is very much like that of the negative temperature
experiment of Purcell and Pound [10].   The coupling of the various
tensors is also apparent and illustrates that the spin temperature
assumption (Boltzmann population restriction throughout decay) is
not valid because B_2 and B_4 become negative.   The time decay is
emphasized by plotting B_k relative to B_k (equilibrium).   The
absolute magnitude of any B_k for $I = 5$ can be obtained from Figure
2.

The first case (x initial = -.3) does not obey the constraint that
at $t = 0$ the observed anisotropy along 0° is given by

$$W(0;0) = 1 + U_2 F_2 B_2 \ (t = 0) + U_4 F_4 B_4 \ (t = 0). \tag{11}$$

The second case (x initial = 0.216) obeys this constraint and now the
structure has disappeared and a monotonic decay is calculated for all
three k's.   This case corresponds to a typical run of Co^{60} in Co
where the observed initial anisotropy corresponds to x = 0.216.   This
assumes a $t = 0$ population distribution corresponding to a Boltzmann
population which is an approximation because of the variation of H_1

as it penetrates the sample and because it is difficult to assume a
fast spin-spin relaxation in very dilute alloys.   The third case
(x initial = 0) is that of saturation or equal populations.   This
would obviously be ideal for obtaining correct T_1 measurements
because complete destruction of all anisotropy (all tensors = 0)
at t = 0.

3. EXPERIMENTAL RESULTS.

Co^{60} in Co fcc was used as an example of the application of this theory. The
sample was a single crystal of Co grown by electro-deposition onto a Cu
single crystal [11]. Co^{60} was codeposited with Co^{59} from a plating bath
to which Co^{60} had been added.   There was a few percent of hcp Co in the
original sample according to X-ray diffractometer measurements but these
were removed by heating to 500°C for approximately thirty seconds and then
quenching in H_2O immediately.   The thickness of the single crystal foil
was about 6000Å which is less than the skin depth in Co at 125 MHz.   After
cooling the sample to .006°K using adiabatic demagnetization of a cerium
magnesium nitrate slurry [12], the resonance was found at 125.10 MHz with
H_o = 600 oe. This is in good agreement with the NMR value for single domain
particler by Gossard et al.[13].   The best linewidth (small modulation) was
1.26 MHz which indicates that there probably was considerable stress in the Co

foil. T_1 measurements were made by modulating over the line with H_1 as

high as experimentally possible in order to maintain the same conditions

over the entire temperature range.   A typical run is shown in Figure 4.

Given that

$$\Delta B_2(t) = \beta_{21}\, e^{-\Lambda_1 t} + \beta_{22}\, e^{-\Lambda_2 t} + \beta_{23}\, e^{-\Lambda_3 t} + \beta_{24}\, e^{-\Lambda_4 t} \quad \text{and}$$

(12)

$$\Delta B_4(t) = \beta_{41}\, e^{-\Lambda_1 t} + \beta_{42}\, e^{-\Lambda_2 t} + \beta_{43}\, e^{-\Lambda_3 t} + \beta_{44}\, e^{-\Lambda_4 t}$$

with the β's coming from the summations in equation (8), then

$$\Delta W\,(0;t) \;=\; U_2 F_2 \Delta B_2\,(t) + U_4 F_4 \Delta B_4\,(t).$$

(13)

The anisotropy curve vs. time included a baseline and a warm-up contribution.

The theory gives the ratio of Λ_1 to Λ_2, Λ_3, Λ_4, so this constraint can be

added, yielding the final function which was least squares fitted to the data:

$$F(t) = P_1 + P_2 t + \Sigma_1\, e^{-\Lambda_1 t} + \Sigma_2 e^{-K_1 \Lambda_1 t} + \Sigma_3 e^{-K_2 \Lambda_1 t} + \Sigma_4\, e^{-K_3 \Lambda_1 t}$$

(14)

where P_1 = base line (equilibrium anisotropy), P_2 = small warm-up contribution,

$\Sigma_1 = U_2 F_2 \beta_{21} + U_4 F_4 \beta_{41}$, etc. and $K_1 = \dfrac{\Lambda_2}{\Lambda_1}$ etc.

The initial conditions used to calculate the β's were taken as the average

of the observed anisotropy during the time H_1 was applied (case 2 in 2.4).

The results of the data fitted by equation (14) with these initial conditions

are shown in Figure 5 which is discussed in the following section.

4. DISCUSSION AND SUMMARY.

The T_1 measurements shown in Figure 5 illustrate the application of the multipole relaxation theory developed in Ref. (9) to NMR/ON. It has been shown that extension to spins higher than one is straight-forward using a computer to do the matrix diagonalization and inversion. The precision of the results is reasonable considering the statistics and also slight initial condition differences between runs. The accuracy depends on correct knowledge of the initial conditions but the smallness of the resonance signal ($\sim$ 25% of anisotropy) probably means the spin levels are not greatly distrubed and thus the initial conditions we have chosen are a good approximation. The Korringa constant, K, from the high-temperature, high-field T_1 measurement of Co^{59} in $Co^{(13)}$ was multi-plied by $[\gamma_n(Co^{60}) / \gamma_n(Co^{59})]^2$ and then $\frac{1}{T_1} = \frac{\hbar\gamma H}{2kK} \coth(x)^*$ was plotted for comparison with our data. The discrepancy may indicate a systematic error in the initial conditions or a deviation from the Korringa Law be-fore reaching our temperatures. We obtain a value of K = 0.55 sec °K which corresponds to the dashed line in Figure 5. Also in Figure 5 we have shown a fit to the same data with a single exponential which illustrates behavior similar to that obtained by Brewer et al. [6] and Co^{60} in Fe. This yields T_1' rather than T_1 and it should be noted that there is apparently no unique relationship between the two. The deviation from

---

* We would like to thank D. A. Shirley for this suggestion. The given ex-pression can be derived from equation (2) in ref. 6 by defining:
$$\frac{1}{\tau} = \tfrac{1}{2}(W_\perp + W_-)$$

$T_1 T$ = constant is still observed in the present theory as expected in a
system obeying Fermi statistics.

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REFERENCES.

1.   F. Bloch, W.W. Hansen and M.E. Packard, Phys. Rev. 70, 474, (1946).
     E.M. Purcell, H.C. Torrey and R.V. Pound, Phys. Rev. 69, 37, (1946).
     B.V. Rollin, Nature 159, 201, (1946).
     A.M. Portis and A.C. Gossard, J. Appl. Phys. 31, 205S, (1960).

2.   E. L. Hahn, Phys. Rev. 80, 580, (1950).
     D.F. Holcomb and R.E. Norberg, Phys. Rev. 98, 1074, (1955).
     M. Weger, A.M. Portis and E.L. Hahn, J. Appl. Phys. 32, 124S (1961).

3.   N.F. Ramsay and R.V. Pound, Phys. Rev. 81, 278 (1951).
     A. Abragam and W.G. Proctor, Phys. Rev. 106, 160, (1957).
     L.C. Hebel and C.P. Slichter, Phys. Rev. 107, 901, (1957).
     A.G. Redfield, Phys. Rev. 98, 1787, (1955).

4.   J.E. Templeton and D.A. Shirley, Phys. Rev. Letters 18, 240, (1967).

5.   D.A. Shirley, Hyperfine Structure and Nuclear Radiations, (North Holland
        Publishing Co., Amsterdam, 1968), pp843 ff.

6.   W.D. Brewer, D.A. Shirley and J.E. Templeton, Phys. Letters, 27A, 81, (1968).

7.   M. Odehnal, J. of Low Temperature Physics, 1, 477, (1969).

8.   P. Jauho and P.V. Pirilä, Phys. Rev. B1, 21, (1970).

9.   H. Gabriel, Phys. Rev. 181, 506, (1969).

10. E.M. Purcell and R.V. Pound, Phys. Rev. 81, 279, (1951).

11. J. Goddard and J.G. Wright, Brit. J. Appl. Phys, 15, 807, (1964); ibid 16,
        1251, (1965).

12. J.A. Barclay, Thesis, University of California, Berkeley, UCLRL No.18986
     (1969).

13.   A.C. Gossard, A.M. Portis, M. Rubinstein and R.H. Lindquist, Phys. Rev. 138A, 1415, (1965).

14.   V. Jaccarino, N. Kaplan, R. E. Walstedt, and J.H. Wernick, Phys. Letters 23, 514, (1966).

Figure 1.   Relaxation factors $G_{1k}{}'$, $G_{2k}{}'$, and $G_{4k}{}'$, vs. t/T_1 for

several values of k' at $X = 0.3$ and $I = 5$.

Figure 2. B_k vs $x = \hbar\omega/2kT$ for $k = 1,2,\ldots\ldots10$.

Figure 3.   Recovery of the tensors, B_k, after three different initial

conditions.   All cases correspond to x (equilibrium) $= 0.3$

and $I = 5$.   The long dash-short dash line is $k = 1$, the

solid line is $k = 2$, and the short dash line is $k = 4$.

The upper case corresponds to x (initial) $= -.3$, the

middle case to x (initial) $= 0.216$, and the lower case to

x (initial) $= 0.0$.

Figure 4.   Anisotropy vs. time for a typical relaxation measurement.

Figure 5.   Experimental relaxation times for Co^{60} in f.c.c. Co. The

solid line represents the extrapolated Co^{59} in Co NMR

results ($K = .75$) [13] and the dashed line is for

$K = .55$ sec °K. The triangles are the data fitted with

a sum of expotentials and the dots are the data fitted with

a single exponential.

Fig. 1

Fig. 2

Fig. 3

RUN 14   CO^{60} in CO fcc
W(WARM) = 26,010
H_1(applied p-p) = 4mOe
H_0 = 1kOe
$\Delta\nu_{FM}$ = 1.2 MHz
ν_{FM} = 500 kHz
I/T = 170°K^{-1}

Fig. 21

Fig. 5