Temperature dependence of the NMR free induction decay in metals

Jerome I. Kaplan*†

Battelle Institute, Columbus, Ohio 43201

W. A. B. Evans

University of Kent at Canterbury, Canterbury, England

(Received 21 January 1974)

A procedure is given for calculating the temperature dependence of the nuclear-spin free-induction decay in a metal. It is shown that interplay between the dipole-dipole interaction and the spin-lattice interaction must be taken into account. A numerical calculation is made for Al.

INTRODUCTION

In this note we will discuss the coupling between the magnetic dipole-dipole interaction and the spin-lattice interaction as evidenced in the temperature dependence of the nuclear-resonance free-induction decay[1] in a metal. To do this, the density-matrix equation which the nuclear-spin system in a metal obeys will first be exhibited; next we will discuss the linewidth as seen in a cw experiment for a two-spin system obeying the aforementioned density-matrix equation; and lastly we will calculate the temperature-dependent free-induction decay for nuclear spins in a metal. Comparison of our results will be made with the temperature dependence of the free-induction decay which has been calculated ignoring the coupling between the dipole-dipole terms and the spin-lattice relaxation.

CALCULATIONS

Applying the Wangness-Bloch[2] and Redfield[3] procedure for obtaining the density-matrix equation of nuclear spins in a metal, one obtains the result that in operator form

$$\dot{\rho} = -i\hbar^{-1}[H,\rho] - \frac{1}{2T_1}\sum_i\sum_\alpha[[\rho-\rho^0, I_i^\alpha], I_i^{-\alpha}] \ , \quad (1)$$

where ρ^0 is the equilibrium distribution function, T_1 is the nuclear relaxation time for a single spin, $\sum_i$ is a sum over all lattice sites,
$$\sqrt{2}\,I_i^{\alpha=1} = I_i^x + iI_i^y, \ I_i^{\alpha=0} = I_i^z, \ \sqrt{2}\,I_i^{\alpha=1} = I_i^x - I_i^y \ ,$$
and

$$H = H_{\text{Zeeman}} + H_{\text{d-d}} + H_{\text{rf}} \ . \quad (2)$$

The dipole-dipole term $H_{\text{d-d}}$ includes any additional interaction such as the Ruderman-Kittel[4] terms. The temperature dependence of T_1 for simple metals is known to be of the form[5]

$$T_1 = a(T_K^\circ)^{-1} \ , \quad (3)$$

where T_K° is temperature in degrees Kelvin.

The usual Bloch-type relaxation form[6] is obtained from Eq. (1) when one evaluates

$$\langle \dot{I}^z \rangle = \text{Tr}\,\rho_{\text{relax}}\,I^z$$

$$=\frac{1}{2T_1}\text{Tr}\sum_\alpha^i\,[\,[\rho-\rho^0 I^\alpha\,]I^{-\alpha}]I^z$$

$$=-\frac{1}{T_1}(\,\langle I^z\rangle - \langle I^z_{\text{equil}}\rangle) \ . \quad (4)$$

One often sees that if two relaxation processes are *uncorrelated* the width arising from both of them can be expressed as

$$\frac{1}{T_{2_{\text{eff}}}} = \frac{1}{T_{2_1}} + \frac{1}{T_{2_2}} \ . \quad (5)$$

The spin-lattice relaxation and the dipole-dipole coupling are not of this nature. The spin-lattice relaxation effectively motionally narrows the dipole-dipole interaction and thus at one and the same time the spin-lattice relaxation reduces the dipole-dipole broadening and creates its own uncertainty broadening. To see this more quantitatively consider the Hamiltonian for the two-spin system:

$$H = \omega_0(I_1^z + I_2^z) + AI_1^z I_2^z + \omega_1(I_1^x + I_2^x)\cos\omega t \ . \quad (6)$$

The resonance condition using Eq. (1) can be calculated as

$$i(\omega - \omega_0) = \frac{3}{2T_1} \pm i\left[\frac{A}{2} - \frac{1}{2}\left(\frac{1}{2T_1}\right)^2\bigg/\frac{A}{2}\right] \quad (7)$$

assuming $A/2 \gg 1/2T_1$. The quantity in square brackets in Eq. (7) exhibits the reduction of the pure ($\pm iA/2$) dipole broadening as previously discussed.

The most accurately calculable property of NMR is the free-induction decay. Several procedures have been advanced to make this calculation,[7] and we have chosen the one[8] which is most easily generalized to include effects arising from the spin-lattice relaxation time.

We start by rewriting Eq. (1) as

$$\dot{\rho} = -i(L_0 + L_1 + L_2)\rho - L_r(\rho - \rho_0) \ , \quad (8)$$

where

$$L_i\rho = [H_i, \rho] \ , \quad (9)$$

$$H_0 = \omega_0\sum_i I_i^z \ , \quad (10)$$

$$H_1 = \sum_{i>j} A_{ij} I_i^{\,z} I_j^{\,z} \quad , \tag{11}$$

$$H_2 = \sum_{i>j} B_{ij} \vec{I}_i \cdot \vec{I}_j \quad , \tag{12}$$

$$L_r(\rho - \rho_0) = \sum_{i,\alpha} [I_i^{\,\alpha}, [I_i^{-\alpha}, \rho - \rho_0]] \quad . \tag{13}$$

Solving Eq. (8) with the initial condition (after 90° pulse) that

$$\rho(0) = \rho^0(90°) \simeq \frac{1 - \hbar \omega_0 I^x}{(2I+1)^N kT} \quad , \tag{14}$$

one obtains

$$\rho = (1 - e^{-i(L_1 + L_2 - iL_r/2T_1)t}) \rho^0$$

$$- \frac{\hbar \omega_0}{(2I+1)^N kT} e^{-i(L_1 + L_2 - iL_r/2T_1)t}$$

$$\times (I^x \cos\omega_0 t + I^y \sin\omega_0 t) \quad . \tag{15}$$

One next substitutes Eq. (15) into

$$M_x = \mathrm{Tr}\, \rho I^x \tag{16}$$

to obtain

$$M_x = \frac{-\hbar \omega_0 \cos\omega_0 t}{(2I+1) kT} \mathrm{Tr}\, I^x\, e^{-i(L_1 + L_2 - iL_r/2T_1)t} I^x \quad . \tag{17}$$

The temperature-independent free-induction decay is obtained by setting $T_1 = \infty$ in Eq. (17), and the temperature-dependent free-induction decay using the relaxation operator in the form

$$-1/T_1(\rho - \rho^0) \tag{18}$$

is obtained by setting $L_r = 2$ in Eq. (17). This latter form of the free-induction decay (FID) will be called uncorrelated FID as opposed to the correlated FID given in Eq. (17) with L_r given in Eq. (13).
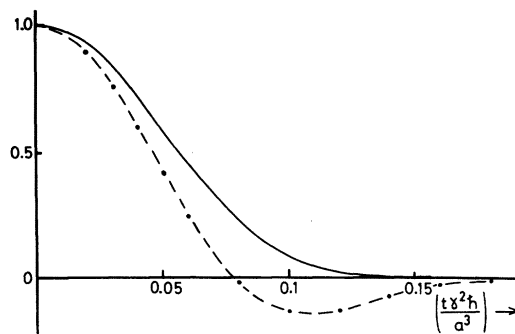

FIG. 1. Plots of the T_1 contributions to the free-induction decay divided by $-t/T_1$ for (i) the correlated case (continuous curve), and (ii) the uncorrelated case (dashed curve). As seen from Eq. (27), the uncorrelated plot is just the Bloch decay curve itself for infinite T_1 evaluated in the approximation $B_0(t) + B_1(t)$. The plots are against the dimensionless time variable $t\gamma^2\hbar/a^3$ $(a^3/\gamma^2\hbar = 1287$ μsec approximately in aluminum).

Equation (17) is evaluated by expanding $\exp[-i(L_1 + L_2 - iL_r/2T_1)t]$ as a power series in L_2 and L_r using the relation that

$$e^{-i(L_1 + L_2 - iL_r/2T_1)t} = e^{-iL_1 t} + e^{-iL_1 t} \int_p^t e^{iL_1 t'}$$

$$\times [-i(L_2 - iL_r/2T_1)] e^{-iL_1 t'} dt' + \cdots . \tag{19}$$

Substituting Eq. (19) into Eq. (17), defining

$$M_x = \frac{-\hbar \omega_0 \cos\omega_0 t}{(2I+1)^N kT} G(t) \quad , \tag{20}$$

and using Eqs. (9) and (13), one obtains

$$G(t) = \mathrm{Tr}\, I^x\, e^{-iH_1 t} I^x e^{iH_1 t} - i\, \mathrm{Tr}\, I^x e^{-iH_1 t} \int_0^t [H_2(t'), I^x] dt'\, e^{iH_1 t}$$

$$- \frac{1}{2T_1} \mathrm{Tr}\, I^x e^{-iH_1 t} \int_0^t \sum_{i,\alpha} [I_i^{\,\alpha}(t'), [I_i^{-\alpha}(t'), I^x]] dt'\, e^{iH_1 t} + \cdots , \tag{21}$$

where

$$A(t) = e^{iH_1 t} A e^{-iH_1 t} \quad . \tag{22}$$

The first two terms in the right-hand side have been previously evaluated for spin-$\frac{1}{2}$ and generalized to arbitrary spin I by Demco,[9] Fornes, Parker, and Memory[10] (N.B., there are minor errors in the published formulas of both these authors). The result for the first two terms which we will call $B_0(t)$ and $B_1(t)$ for the general spin case is

$$B_0(t) = \prod_{j(\neq i)} \frac{\sin[A_{ij} t(I + \frac{1}{2})]}{(2I+1)\sin\frac{1}{2} A_{ij} t} \quad , \tag{23}$$

$$B_1(t) = \frac{1}{3} \sum_{j(\neq i)} A_{ij} \sin\frac{1}{2} A_{ij} t \left(\frac{t F_{ij}(t)}{2I+1} \prod_{k(\neq i,j)} \frac{\sin[A_{ik} t(I + \frac{1}{2})]}{(2I+1)\sin\frac{1}{2} A_{ik} t} \right.$$

$$\left. - \frac{3}{2} \int_0^t dt'\, \frac{F_{ij}(t-t')F_{ij}(t')}{I(I+1)(2I+1)^2} \prod_{k(\neq i,j)} \frac{\sin\{[A_{ik}(t-t') + A_{jk} t'](I + \frac{1}{2})\}}{(2I+1)\sin\{\frac{1}{2}[A_{ik}(t-t') + A_{jk} t']\}} \right) \quad , \tag{24}$$

where

$$F_{ij}(t) = \frac{\sin I A_{ij} t}{2 \sin^3(\frac{1}{2} A_{ij} t)} - \frac{I \cos[A_{ij} t(I + \frac{1}{2})]}{\sin^2(\frac{1}{2} A_{ij} t)} \quad . \tag{25}$$

In the above formulas the interaction between the nuclear spins is taken to be solely dipolar in character. With these definitions one evaluates Eq. (17) and obtains for the correlated FID

$$G_c(t) = B_0(t) + B_1(t) - \frac{t B_0(t)}{2 T_1} \left[2 - \sum_{j\,(\neq i)} \frac{\sin(A_{ij} t) F_{ij}(t)}{\sin[A_{ij} t(I + \frac{1}{2})]} \left(1 - \frac{\tan \frac{1}{2} A_{ij} t}{\frac{1}{2} A_{ij} t} \right) \right] \quad . \tag{26}$$

The uncorrelated FID is

$$G_{uc}(t) \simeq [B_0(t) + B_1(t)] (1 - t/T_1) + \cdots \quad . \tag{27}$$

The T_1 contribution divided by $(-t/T_1)$ to G_c and G_{uc} is plotted in Fig. 1 for the case of an aluminum polycrystal which is a fcc lattice of spin-$\frac{5}{2}$ nuclei. For a polycrystal one has to average the above expressions over all angles. In our work, because

of cubic symmetry, the angle average coincides with

$$\langle B \rangle = \frac{12}{\pi} \int_0^{\pi/4} d\phi \int_{\cos\phi/(1+\cos^2\phi)^{1/2}}^1 d(\cos\theta) B(\phi, \theta) \tag{28}$$

which is the average over the spherical triangle joining the direction points (100), (110), and (111), i.e., one sixth of an octant.

---

[1]A. Abragam, *Principles of Nuclear Magnetism* (Oxford U. P., Oxford, 1961), Chap. IV.

[2]R. K. Wangness and F. Bloch, Phys. Rev. 89, 728 (1953).

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

[4]M. A. Ruderman and C. Kittel, Phys. Rev. 96, 99 (1954).

[5]J. Korringa, Physica 16, 601 (1950).

[6]F. Bloch, Phys. Rev. 70, 460 (1946).

[7]I. J. Lowe and R. E. Norberg, Phys. Rev. 107, 46 (1957); J. Tjon, Phys. Rev. 143, 259 (1966); P. Resibois, P. Borckmans, and D. Walgraef, Phys. Rev. Lett. 17, 1290 (1966).

[8]W. A. B. Evans and J. G. Powles, Phys. Lett. A 24, 218 (1967).

[9]D. Demco, Phys. Lett. A 27, 702 (1968).

[10]R. E. Fornes, G. W. Parker, and J. D. Memory, Phys. Rev. B 1, 4228 (1970).