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Nuclear Spin-Lattice Relaxation in Pure and Impure Indium. I. Normal State*

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Transient nuclear spin-lattice relaxation measurements have been made in indium metal and the *In*Cd, *In*Tl, *In*Sn, and *In*Pb dilute alloy systems, using the In^{115} nuclear-quadrupole-resonance (NQR) spectrum. The theory of spin-lattice relaxation in NQR is described for both magnetic and quadrupolar contributions to the relaxation. Precautions were taken to avoid eddy-current heating. A slight dependence of the relaxation rate on NQR transition was observed. Several explanations of this effect were considered, none of which proved satisfactory. In particular, no evidence was found for quadrupolar relaxation. The relaxation rate increased in the alloys at a rate of a few percent/(at.% solute) for all alloy systems studied. No extrema in relaxation rate in the concentration range 0.5–1-at.% solute were found, in contrast to the behavior of the Knight shift as measured by Hewitt and co-workers. The observed increase in relaxation rate in the alloys may be due either to increased enhancement of the contact relaxation, or to an increase in the noncontact contribution to the total relaxation rate.

I. INTRODUCTION

Pure nuclear quadrupole resonance (NQR) has seldom been employed in the study of nuclear spin-lattice relaxation in solids, since in general the relaxation of the spin system to equilibrium with the lattice is not exponential and its analysis is rather complicated.[1,2] In spite of this difficulty, the investigation of spin-lattice relaxation (SLR) using NQR is useful when the NQR spectrum is well defined and when the static quadrupole interaction broadens the ordinary NMR line severely. The latter circumstance makes a precise NMR measurement of the relaxation time T_1 difficult.[3] We report in this paper the results of SLR measurements at 4.2 K in indium metal and dilute *In*Cd, *In*Tl, *In*Sn, and *In*Pb alloys, and their interpretation in terms of the current understanding of nuclear relaxation mechanisms in metals. A preliminary account of the results for pure In has been published elsewhere.[2]

The motivation for this work was twofold. First, the 96%-abundant In^{115} nuclei possess a large quadrupole moment Q, and in addition the In Fermi surface is expected to possess considerable non-s character.[4–6] Under these circumstances the possibility exists that a portion of the observed SLR, hereafter referred to as QSLR, is due to the interaction between the nuclear quadrupole moments and fluctuations in the electric field gradient at the nuclear sites.[4,7] Measurement of the quadrupolar relaxation rates W_{Q1} and W_{Q2} (to be defined below) would therefore provide information on the symmetry of the conduction electrons at the In Fermi surface. Furthermore, SLR measurements in the superconducting state of indium[8] require for their interpretation an estimate of the ratio of QSLR to magnetic SLR (MSLR), since in general the influence of superconductivity on the relaxation rate is expected to be different for the two processes.[9] The existence of a large noncontact relaxation rate in liquid In (and by inference in solid In, since the relaxation-time–temperature product T_1T is not greatly affected by melting) has been reported by Warren and Clark,[10] and it is of interest to determine how much, if any, of the additional relaxation at low temperatures is quadrupolar. If there are two or more NQR transitions ($I>\frac{3}{2}$), QSLR can in principle be separated from MSLR since, as discussed below in Secs. II and III, the recovery of the spin systems depends on the observed transition in such a way that the contribution of QSLR may be extracted.

The second motivation for the present work was provided by the results of the extensive series of Knight-shift measurements in In-based alloys carried out by Hewitt and co-workers.[11,12] A pronounced minimum in the solute concentration dependence of the Knight shift was observed for solute concentrations in the range 0.5–1 at.%. It is clear that knowledge of the SLR behavior in this concentration range would clarify the origin of the Knight-shift minimum.

Measurements were made at temperatures near 4.2 K on three of the four zero-field In^{115} ($I=\frac{9}{2}$) NQR lines.[13,14] (The signal from the transition of lowest frequency was too weak to permit accurate SLR measurements.) The time dependence of the observed relaxation could always be fitted to good accuracy by a sum of terms exponential in the time between saturation of the line and observation of the recovery. The theory of such multiexponential relaxation is treated in Sec. II, and the experimental procedure is described in Sec. III. Section IV gives the results and a discussion of their interpretation, and conclusions are presented in Sec. V. Briefly, we found that (i) the data were consistent with purely magnetic relaxation to within experimental error; (ii) a slight dependence of the relaxation time T_1 on spectral line was observed, which could be attributed neither to quadrupolar relaxation nor to any other plausible mechanism; (iii) the temperature-independent quantity T_1T decreased slightly as a function of solute concentration in all alloy systems studied, at a rate of the order of a few percent/(at.% solute); and (iv) no evidence of an extremum in T_1T corresponding to the Knight-shift minimum was seen. This latter result is contrary to an earlier conclusion, quoted in Ref. 12, which was subsequently found to be in error.

II. MULTIEXPONENTIAL RELAXATION IN NQR

A. Master Equation

The static quadrupolar Hamiltonian for an axially symmetric field gradient and half-integer nuclear spin may be written

$$\mathcal{H}_Q = \tfrac{1}{2}\hbar\omega_Q[I_z^2 - \tfrac{1}{3}I(I+1)] , \qquad (1)$$

where[15]

$$\hbar\omega_Q = \frac{3e^2qQ}{2I(2I-1)} . \qquad (2)$$

For pure In metal $\omega_Q/2\pi = 1.886 \pm 0.002$ MHz.[14] The energy eigenvalues of $\mathcal{H}_Q$ are

$$E_m = \tfrac{1}{2}\hbar\omega_Q[m^2 - \tfrac{1}{3}I(I+1)] , \qquad (3)$$

and there is a twofold Kramers degeneracy between states $I_z = \pm m$.

In NQR a radio-frequency (rf) magnetic field is applied to the sample at the transition frequency ω_r. (The subscript r will be used consistently as the index of the observed transition.) From Eq. (3) we have

$$\omega_r = (E_r - E_{r-1})/\hbar = \omega_Q(r - \tfrac{1}{2}) . \qquad (4)$$

Thus there are $(I - \frac{1}{2})$ spectral lines, at the frequencies $\omega_Q, 2\omega_Q, \ldots, (I-\frac{1}{2})\omega_Q$.

The energy levels given by Eq. (3) are not equally spaced, and it is this circumstance which gives rise to multiexponential relaxation. In the case of equally spaced levels, as in ordinary NMR, spin-spin interactions between neighboring nuclei are capable of altering the level populations, and it has been hypothesized with a great deal of success that such spin-spin interactions establish a unique temperature within the spin system.[15,16] If internal equilibration takes place in a time much shorter than that required for equilibration between the spin system and its surroundings, as is often the case in solids at low temperatures, then the latter process can be shown to take place exponentially.[15,16] This is not the case in NQR, since the inequality of the level spacing means that only those spin-spin processes which leave the populations unchanged conserve energy.

Under these circumstances it is generally accepted that after an initial disturbance the populations relax to thermal equilibrium following a "master" rate equation of the form

$$\frac{dp_m}{dt} = \sum_{n=-I}^{I} W_{mn}(p_n - p_m) , \qquad (5)$$

where the p_m are defined to be the deviations of the level populations from their equilibrium values.[15] The transition probabilities W_{mn} and W_{nm} are then equal by the principle of detailed balance.

A number of workers have considered the solution of the master equation for the case where the Zeeman-level spacing is rendered unequal by a small quadrupolar splitting.[3,17,18] The solution in this case is most easily displayed by forming the population differences

$$u_m = p_m - p_{m-1} , \qquad (6)$$

and writing the master equation for the vector $\vec{u}$ as

$$\frac{d\vec{u}}{dt} = -\underline{A}\vec{u} . \qquad (7)$$

It is then easy to see that the solution is of the form

$$\vec{u}(t) = e^{-\underline{A}t}\vec{u}(0) . \qquad (8)$$

We shall call $\underline{A}$ the relaxation matrix.

In NQR the $\pm m$ degeneracy, together with the use of a linearly polarized rf magnetic field, introduces the additional constraint that the population differences observed by NQR are not given by Eq. (6), but rather by

$$u_m = (p_m - p_{m-1}) + (p_{-m} - p_{-m+1}) . \qquad (9)$$

That is, only the total population difference for the two degenerate manifolds is observable.[15] We take m to be positive in Eq. (9) and the following. Equation (9) defines the total population difference $u_m(t)$. From Eq. (5) we find the rate equation for the $u_m(t)$ to be

$$\frac{du_m}{dt} = \sum_n [W_{mn}(p_n - p_m) + W_{-m,n}(p_n - p_{-m}) - W_{m-1,n}(p_n - p_{m-1}) - W_{-m+1,n}(p_n - p_{-m+1})] . \qquad (10)$$

It is useful to change the summation index from n to $m+q$, so that

$$\frac{du_m}{dt}=\sum_q\big[W_m^{(q)}(p_{m+q}-p_m)+W_{-m}^{(-q)}(p_{-m-q}-p_{-m})$$
$$-W_{m-1}^{(q)}(p_{m-1+q}-p_{m-1})-W_{-m+1}^{(-q)}(p_{-m+1-q}-p_{-m+1})\big]\,, \tag{11a}$$

with

$$W_m^{(q)}=W_{m,m+q}\,. \tag{11b}$$

Now it can be verified directly for the transition probabilities involved in both MSLR and QSLR that

$$W_m^{(q)}=W_{-m}^{(-q)}\,, \tag{12}$$

so that if we define

$$P_m=p_m+p_{-m}\,, \tag{13}$$

then

$$\frac{du_m}{dt}=\sum_q W_m^{(q)}(P_{m+q}-P_m)-W_{m-1}^{(q)}(P_{m-1+q}-P_{m-1})\,. \tag{14}$$

Equation (14) can be written, using $u_m=P_m-P_{m-1}$, as

$$\frac{du_m}{dt}=\left(\sum_{q>0}\sum_{s=1}^{q}+\sum_{q<0}\sum_{s=q+1}^{0}\right)v(m,\,q,\,s)\,, \tag{15a}$$

with

$$v(m,\,q,\,s)=W_m^{(q)}u_{m+s}-W_{m-1}^{(q)}u_{m-1+s}\,, \tag{15b}$$

and where $m=I,\ I-1,\ldots,\frac{5}{2},\ \frac{3}{2}$.

B. Relaxation Matrices for First- and Second-Kind Processes

We can classify the transition probabilities according to the values of q for which $W_m^{(q)}\neq 0$. This classification corresponds to the usual selection rule for the process involved. For MSLR, $q=\pm 1$. For QSLR, there are two processes, $q=\pm 1$ and $q=\pm 2$.[1]

For $q=\pm 1$, Eqs. (15) reduce to

$$\frac{du_m}{dt}=W_m^{(1)}u_{m+1}-2\,W_{m-1}^{(1)}u_m+W_{m-2}^{(1)}u_{m-1}\,, \tag{16}$$

so that the relaxation matrix elements corresponding to this first-kind relaxation process are

$$A_{m,m+1}^{(1)}=-W_m^{(1)}\,, \tag{17a}$$

$$A_{mm}^{(1)}=2\,W_{m-1}^{(1)}\,, \tag{17b}$$

$$A_{m,m-1}^{(1)}=-W_{m-2}^{(1)}\,. \tag{17c}$$

For a second-kind process, $q=\pm 2$, Eqs. (15) lead to

$$A_{m,m+2}^{(2)}=-W_m^{(2)}\,, \tag{18a}$$

$$A_{m,m+1}^{(2)}=-W_m^{(2)}+W_{m-1}^{(2)}\,, \tag{18b}$$

$$A_{mm}^{(2)}=W_{m-1}^{(2)}+W_{m-2}^{(2)}\,, \tag{18c}$$

$$A_{m,m-1}^{(2)}=W_{m-2}^{(2)}-W_{m-3}^{(2)}\,, \tag{18d}$$

$$A_{m,m-2}^{(2)}=-W_{m-3}^{(2)}\,. \tag{18e}$$

C. Magnetic and Quadrupolar Relaxation Matrices

The transition probabilities for MSLR and for first- and second-kind QSLR processes can be written as

$$W_{mn}^{M}=W_M(|\langle m|\,I_+|n\rangle|^2+|\langle m|\,I_-|n\rangle|^2)\,, \tag{19}$$

$$W_{mn}^{Q1}=W_{Q1}(|\langle m|\,I_zI_++I_+I_z|n\rangle|^2$$
$$+|\langle m|\,I_zI_-+I_-I_z|n\rangle|^2)\,, \tag{20}$$

$$W_{mn}^{Q2}=W_{Q2}(|\langle m|\,I_+^2|n\rangle|^2+|\langle m|\,I_-^2|n\rangle|^2)\,. \tag{21}$$

From these relations and from the well-known properties of the angular momentum operators,[19] the relaxation matrices for any I can be obtained using Eqs. (11b), (17), and (18).

D. Exact Solutions of Master Equation

The exact solution [Eq. (8)] of Eq. (7) can be written

$$u_m(t)=\textstyle\sum_i \alpha_{mi}\,a_i\,e^{-\lambda_i t}\,, \tag{22}$$

where the λ_i are the $(I-\frac{1}{2})$ nondegenerate eigenvalues of the relaxation matrix $\underline{A}$ and the α_{mi} are the corresponding eigenvectors, normalized arbitrarily. The a_i are then fixed by the initial conditions

$$u_m(0)=\textstyle\sum_i \alpha_{mi}\,a_i \tag{23}$$

or

$$a_i=\textstyle\sum_m \alpha_{im}^{-1}\,u_m(0)\,. \tag{24}$$

The solution given by Eq. (22) is independent of the normalization of α_{mi}, since if $\alpha_{mi}\to\eta_i\alpha_{mi}$, $\alpha_{im}^{-1}\to\eta_i^{-1}\alpha_{im}$ and the product $\alpha_{mi}\,a_i$ is invariant. Values of α_{mi} and α_{im}^{-1} are given in Appendix A for pure MSLR.

E. Initial Conditions

In the experiments to be described below, the spin system was allowed to come to equilibrium and then prepared by the application of a single rf pulse of effective tipping angle θ to the rth transition.[15] The resultant initial conditions are found to be

$$u_r(0)=\Gamma_r\,, \tag{25a}$$

$$u_{r+1}(0)=u_{r-1}(0)=-\tfrac{1}{2}\Gamma_r=-\tfrac{1}{2}u_r(0), \tag{25b}$$

where in the high-temperature limit $k_BT\gg\hbar\omega_Q$,

$$\Gamma_r=(\hbar\omega_r/k_BT)(1-\cos\theta)\,. \tag{26}$$

The rth transition population difference $u_r(t)$ was

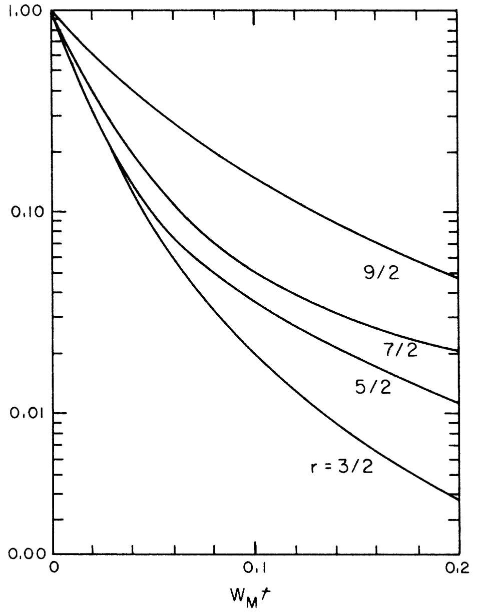

FIG. 1. Dependence of the population difference $u_r(t)$ on relaxation rate W_M, time t, and transition index r, for $u_r(0)=1$, $I=\frac{9}{2}$, and pure magnetic relaxation. The theory of this dependence is discussed in the text.

then monitored as it recovered to equilibrium $u_r(\infty)=0$. For these initial conditions, which are not the most general but which are the simplest to apply experimentally, the normalizing coefficients become, from Eq. (24),

$$a_i=[\alpha^{-1}_{ir}-\tfrac{1}{2}(\alpha^{-1}_{i,r+1}+\alpha^{-1}_{i,r-1})]\,u_r(0)\ . \tag{27}$$

We note that the value of θ enters the a_i only in the multiplicative constant $u_r(0)$, and that the functional form of $u_r(t)$ is independent of $u_r(0)$, and hence of θ. Values of $b_{ri}=\alpha_{ri}a_i/u_r(0)$ are given in Appendix B for $I=\frac{5}{2}$, $\frac{7}{2}$, and $\frac{9}{2}$.[20]

We note that in general the initial conditions are well defined as long as (i) the entire resonance line is uniformly saturated by the initial rf pulse, and (ii) the lines are not so broad that their "tails" overlap appreciably. Both conditions are considerably easier to fulfill in NQR than in quadrupolar-broadened NMR, and experimentally it appears that a NQR line may be rather severely broadened by a static distribution of quadrupole interactions without introducing too much error.

Figure 1 gives the dependence of $u_r(t)$ on $W_M t$ and r, for $u_r(0)=1$, $I=\frac{9}{2}$, and pure MSLR. If the relaxation time T_1 is defined by $T_1^{-1}=2W_M$, to correspond with the usual T_1 measured using NMR, it can be seen from Fig. 1 that the $1/e$ time for the relaxation curves varies from ~ $0.04T_1$ to ~ $0.1T_1$ for the various transitions.

F. Solution for Pure MSLR: Perturbation Theory for a Small Admixture of QSLR

In general the relaxation matrix is the sum of three terms:

$$\underline{A}=\underline{A}^{(M)}+\underline{A}^{(Q1)}+\underline{A}^{(Q2)}\ . \tag{28}$$

It is difficult to diagonalize $\underline{A}$ for arbitrary values of W_M, W_{Q1}, and W_{Q2}. An alternative procedure is to treat the quadrupolar terms as small perturbations on a dominant magnetic term. The applicability of such a procedure to a given experimental situation must be decided in a self-consistent manner.

Our treatment parallels the standard time-dependent perturbation theory of the Schrödinger equation. We let the zeroth-order solution be given by Eq. (22) for $\underline{A}=\underline{A}^{(M)}$, i.e., $\lambda_i=\lambda_i^M$. Then

$$u_m^{(0)}(t)=\textstyle\sum_i \alpha_{mi}a_i e^{-\lambda_i^M t}\ . \tag{29}$$

The exact solution $u_m(t)$ is generated by allowing the constants a_i to vary with time:

$$u_m(t)=\textstyle\sum_i \alpha_{mi}a_i(t)e^{-\lambda_i^M t}\ . \tag{30}$$

From Eqs. (7), (28), and (30) we can form a differential equation for the $a_i(t)$. With $\underline{A}^{(Q)}=\underline{A}^{(Q1)}+\underline{A}^{(Q2)}$,

$$\sum_k \alpha_{mk}\frac{da_k}{dt}e^{-\lambda_k^M t}=-\sum_n A_{mn}^{(Q)}\sum_j \alpha_{nj}a_j e^{-\lambda_j^M t}\ . \tag{31}$$

Multiplication from the left by α^{-1}_{im} and summation over m gives

$$\frac{da_i}{dt}=-\sum_j A_{ij}^{(Q)}a_j e^{(\lambda_i^M-\lambda_j^M)t}\ , \tag{32}$$

with

$$A_{ij}^{(Q)}=\sum_{mn}\alpha^{-1}_{im}A_{mn}^{(Q)}\alpha_{nj}\ . \tag{33}$$

Equation (32) is exact. To first order, direct integration yields

$$\alpha_i^{(1)}(t)=-A_{ii}^{(Q)}a_i^{(0)}t-\sum_{j\neq i}A_{ij}^{(0)}a_j^{(0)}\frac{(e^{(\lambda_i^M-\lambda_j^M)t}-1)}{(\lambda_i^M-\lambda_j^M)}\ , \tag{34}$$

so that if we set

$$u_m(t)\approx u_m^{(0)}+u_m^{(1)}\ , \tag{35}$$

we have

$$u_m^{(1)}(t)=-\sum_i\left(A_{ii}^{(Q)}a_i^{(0)}t\,e^{-\lambda_i^M t}+\sum_{j\neq i}A_{ij}^{(Q)}a_j^{(0)}\frac{(e^{-\lambda_j^M t}-e^{-\lambda_i^M t})}{(\lambda_i^M-\lambda_i^M)}\right). \tag{36}$$

We see that although $a_i^{(1)}(t)$ diverges for large t, the correction term $u_m^{(1)}(t)$ is well behaved.

III. EXPERIMENTAL

The experimental work described in this section and Sec. IV was carried out in two laboratories: the Atomic Energy Research Establishment, Harwell, and the University of California, Riverside. To within experimental error no difference could be found between corresponding results obtained at the two locations.

A. Samples

The In and *In*Pb samples prepared and investigated at Harwell have been described previously.[8] The In, *In*Cd, *In*Tl, *In*Sn, and *In*Pb samples in experiments at Riverside were described by Anderson *et al.*[11] and by Thatcher and Hewitt.[12] The solid solubility of Cd, Tl, Sn, and Pb in In is well established for dilute solute concentrations, and no difficulty with sample preparation or maintenance was experienced.

B. Spectrometry

A transient NMR-NQR spectrometer was used for the experiments at both Harwell and Riverside. Phase-coherent detection was employed, and the signal-to-noise (S/N) ratio was increased after detection by a "boxcar" gated integrator. S/N ratios of 100–200 were obtained after integration in the most favorable cases. A spin-echo $\pi/2$-π pulse sequence was used to observe the signal in all cases except that of pure In, where a free-induction signal could be obtained after a single $\pi/2$ pulse.[21] The difference signal between the echo (or free-induction) amplitude $S_r(t)$, a time t after the initial saturating pulse, and a reference $S_r(t\rightarrow\infty)$, was recorded. This difference signal $V_r(t)=S_r(t)-S_r(\infty)$ is proportional to the population difference $u_r(t)$ discussed in Sec. II. The effect of long-term spectrometer drift was minimized by this procedure. There was a small but non-negligible 60-Hz baseline modulation in the output of the Riverside spectrometer, and all observation sequences were triggered synchronously with a 60-Hz phase reference to eliminate the effect of the modulation on the signal data. Departures from linearity of the receiving-system characteristics were determined to be less than 0.5%

A single saturating pulse was used, instead of the more usual train of several saturating pulses.[3] This procedure was necessitated by the short $1/e$ time (~ 1–2 msec at 4.2 K) of the signal recovery after saturation. The minimum time between pulses in a saturating pulse train is of the order T_2, the echo-envelope decay time, which was observed to be ~ 50–150 μsec depending on sample and transition. Thus, appreciable relaxation would have occurred between the pulses of the train, and the coefficients a_i after the last saturating pulse would no longer have been given by Eq. (27). In principle, the a_i could be computed using a self-consistent value of T_1 to describe relaxation betweer the saturating pulses. It was felt that the use of only one saturating pulse, and the restriction of measurements to systems where the line was sufficiently narrow to be adequately spanned by the Fourier transition of the pulse shape, gave more reliable results. Pulsed rf fields of amplitude $2H_1\approx 150$–250 G were produced by the gated-amplifier transmitter, and a minimum pulse duration of ~ 0.7 μsec was required for a $\pi/2$ pulse. The Fourier-transform half-width is about 250 kHz for such a pulse. Measurements were made for the most part on samples for which the linewidth was of this order of magnitude or smaller. This restriction limited the maximum solute concentration in the alloys to about 2 at.% for Cd, Sn, and Pb solutes, and to about 3 at.% for Tl solute. Some measurements were made at higher concentrations. Some anomalies in T_1T were observed at high solute concentrations.

In ordinary NMR, inaccuracy due to inadequate saturation can be attributed to either of two causes: (i) unequally spaced levels due to a quadrupolar splitting,[3] or (ii) cross relaxation between nuclei contributing to different portions of an inhomogeneously broadened line.[22] In the analysis of pure NQR experiments the effect of unequally spaced levels has been taken into account from the beginning, but the possibility of cross relaxation remains.

Two qualitative checks on the effect of cross relaxation were made. First, the observed relaxation rate varied only slightly, if at all, when the saturating pulse length was changed by ~ 50%, for all samples and transitions. Increasing the pulse length decreases the width of its Fourier transform, and if cross relaxation were important, its effect should be increased by the resulting nonuniform saturation. Second, there was no observable dependence of the relaxation rate on small changes of spectrometer frequency. Again, if cross relaxation were important, its effect would be expected to depend on the frequency within the line.

C. Transverse SLR

The short relaxation times encountered in indium raise a subtle question concerning the data analysis. As is well known in more usual resonance experiments, lifetime broadening of the nuclear spin levels by spin-lattice relaxation contributes to the homogeneous linewidth,[15] and thus shortens the spin-echo-envelope lifetime T_2. We shall call this effect "transverse SLR." Now, the spectrometer receiving system requires a finite time t_d to "recover" from the effect of the rf pulse(s), and therefore observations of the signal amplitude must be

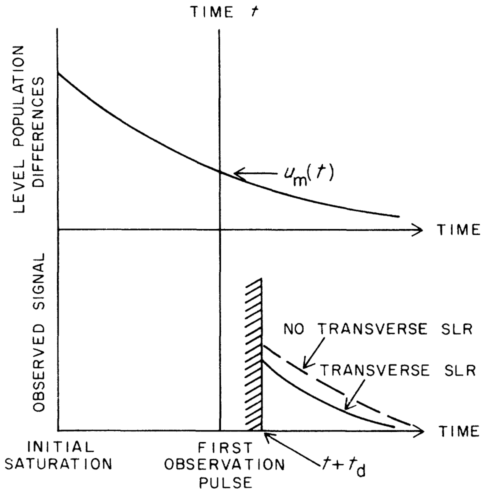

FIG. 2. Schematic representation of the effect of transverse spin-lattice relaxation on the signal obtained in a longitudinal SLR measurement.

made at a time longer than t_d after the initial $\pi/2$ pulse. If appreciable transverse SLR occurs during this time, it will contribute to the signal amplitude as depicted schematically in Fig. 2. In ordinary NMR, this effect, if present, changes the signal amplitude by a constant factor, since the form of the transverse SLR is independent of the level populations just before the observation. We have seen in Sec. II E, however, that the form of the *longitudinal* SLR response (i.e., the relative contributions of the various exponential terms) depends strongly on the initial conditions. For transverse SLR in quadrupole resonance, the initial conditions depend in general on the various $u_m(t)$ just before the observation, and the form of the transverse SLR might be expected to vary with t in such a way as to add a small, but possibly non-negligible, spurious time dependence to the signal $V_r(t)$.

We have investigated this possibility theoretically by calculating (i) the density matrix $\rho(0_+)$ immediately after a rf pulse of length t_w, under the assumption that ρ is diagonal immediately before the pulse; and (ii) the effect of transverse SLR on the time evolution of ρ after the pulse. Only the off-diagonal elements of ρ contribute to the signal. The result of these calculations is that (i) those off-diagonal elements $\rho_{r,r-1}=\rho^*_{r-1,r}$ which correspond to the observed transition are of order $\omega_r t_w/\theta$ (~25–50 times) larger than all other off-diagonal elements, and that (ii) to this order the observed signal in the presence of transverse SLR does not depend on t other than via the desired proportionality to $u_r(t)$. Like longitudinal SLR, transverse SLR is in general multiexponential. In the absence of an unambiguous observation of the effect, the coefficients have not been calculated.

D. Cryogenics

Vapor-pressure thermometry and the T_{58} vapor-pressure temperature scale[23] were used to determine the sample temperature. Nearly all experiments were carried out at temperatures in the vicinity of 4.2 K. A few measurements were also made at $T\approx 3.45$ K, just above the superconducting transition. No temperature dependence of the relaxation was observed other than the expected linear scaling. This result is consistent with the supposition that the relaxation is dominated by Fermi-surface conduction electrons.[24]

The favorable S/N ratio, along with the high electrical conductivity of the samples, led us to undertake rather extensive precautions to reduce to below the experimental error the effect of eddy-current heating by the high-power rf pulses. The shield can which enclosed the sample and sample coil was changed from brass to stainless steel to reduce its electrical conductivity. The original glass sample vials were exchanged for perforated Mycarta plastic holders, shown in Fig. 3(a), in which the powder samples were retained by a cylinder of coarse filter paper. The sample coil was wound on a form consisting of four dowels, as shown in Fig. 3(b). The loss in filling factor was tolerated in return for the greater ease of convective cooling by the liquid helium in which the sample was immersed. The powdered samples were not mixed with any binder substance, to allow liquid He to circulate as freely as possible between the powder grains. A sample consisting of 50% pure In powder and 50% KCl powder by volume was fabricated, to test the possibility that electrical contact between sample particles increased the heating. No differences in behavior between this sample and a pure In-powder sample could be observed.

Before the above precautions were taken, the observed relaxation was more rapid when any of the following three quantities was increased: rf pulse amplitude $2H_1$, rf pulse width(s) t_w, and the repetition rate of the entire measurement sequence. The

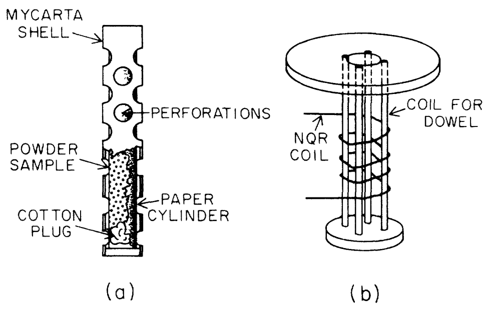

FIG. 3. (a) Perforated sample holder. (b) Open-construction sample coil.

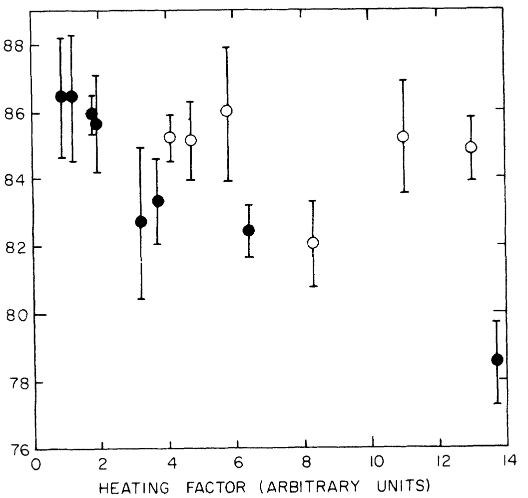

FIG. 4. Dependence of the quantity T_1T on heating factor, defined in the text, before and after modifications designed to reduce eddy-current heating and increase convective cooling of the sample. Closed circles indicate data taken before modifications; and open circles, data taken after modifications. The error bars indicate the 90% confidence level.

relaxation-time-temperature product T_1T, obtained from the data as described in Sec. III E below, depended on a heating factor, defined by

$$(\text{heating factor}) = (\text{repetition rate}) \times H_1^2 \sum_{\text{pulses}} t_w \; , \quad (37)$$

as shown in Fig. 4 for the $r = \frac{9}{2}$ transition in pure In. Data are also shown in Fig. 4 which were taken after the above modifications were made. The improvement was slight but perceptible, and, more importantly, no appreciable systematic dependence of T_1T on the heating factor was discernible after modification. This latter result leads us to conclude tentatively that our results are characteristic of zero heating.

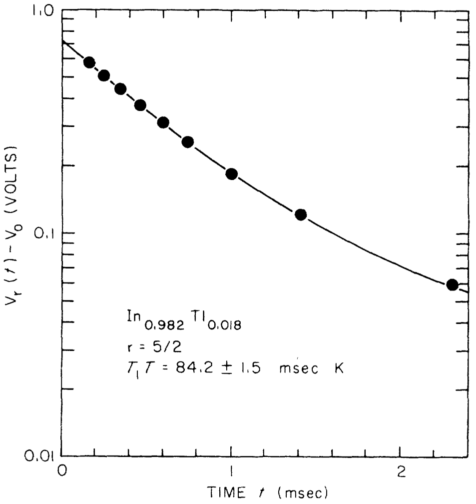

FIG. 5. Relaxation data for an *In*Tl alloy. The circles are experimental points, and the curve is the best theoretical fit. The experimental error is nowhere greater than the circle radii.

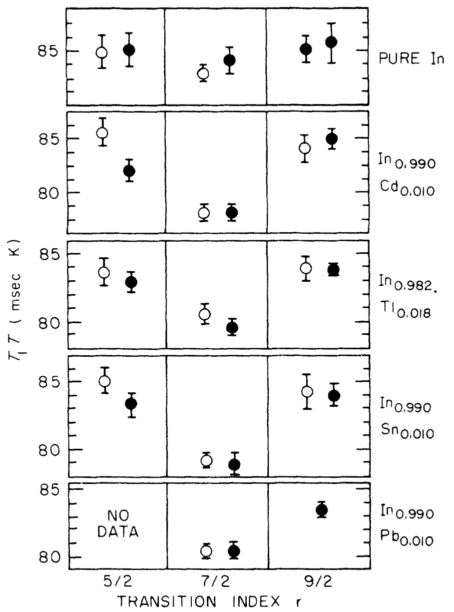

FIG. 6. Sample and transition dependence of T_1T. Closed circles indicate data taken with "long" ($\gtrsim 1.5\,\mu$sec) saturating pulses. Open circles indicate data taken with "short" ($\lesssim 1\,\mu$sec) saturating pulses.

E. Data Analysis

In practically all measurements the values of time interval t between saturation and observation were chosen so that the resulting $V_r(t)$ were approximately equally spaced from minimum to maximum values. An effective relaxation time T_1 was defined by a three-parameter least-squares fit of the data to the following expression for $V_r(t)$:

$$V_r(t) = V_0 + (V_1 - V_0)\, u_r^{(0)}(t/T_1) \; . \quad (38)$$

Here V_0 is the equilibrium signal for $t \gg T_1$ ($V_0 \neq 0$ because of an arbitrary zero shift in the data recording arrangement), and V_1 is the signal extrapolated to $t = 0$. $u_r^{(0)}(t/T_1)$ is given by Eq. (29). V_0, V_1, and T_1 were varied for the best fit. The standard deviations of these parameters were calculated in the course of the fit and were used to compute the 90% confidence-level error bars shown in Fig. 4 and subsequent data figures. The error in V_0 and V_1 varied between ± 0.5% and ± 1% and that in T_1 between ± 1% and ± 2%, for those measurements where no systematic source of error could be identified. This good accuracy, together with the fact

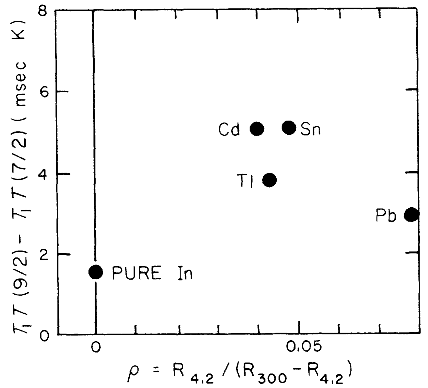

FIG. 7. Correlation of difference in T_1T between the $r=\frac{9}{2}$ and $r=\frac{7}{2}$ transitions with sample residual resistivity ratio ρ.

that the value of T_1 obtained did not depend greatly on r for a given sample (the observed dependence, of the order of a few percent, will be discussed in Sec. IV A), confirms our hypothesis that MSLR is dominant in In and its dilute alloys. An example of the fit obtained is shown in Fig. 5 for the alloy $In_{0.982}Tl_{0.018}$.

IV. EXPERIMENTAL RESULTS AND DISCUSSION

A. Transition Dependence of T_1T

Figure 6 gives the dependence on transition of the quantity T_1T, obtained as described in Sec. III, for pure In and four In-based alloys. It is clear that for $r=\frac{7}{2}$, T_1T is systematically a few percent smaller than for the other two transitions observed.[25] The difference $T_1T(\frac{9}{2}) - T_1T(\frac{7}{2})$ is given in Fig. 7 as a function of the residual resistivity ratio $\rho = R_{4.2}/(R_{300}-{}_{4.2})$, calculated from the nominal solute concentration c and the measured values of ρ/c taken from Chanin *et al.*[26] While the effect is larger for the alloys than for pure In, the observed ρ dependence is not monotonic. This result has a bearing on possible explanations of the anomaly as discussed below. The effect is probably not due to experimental procedure or data analysis. Considerable care was excercised to ensure that the results were independent of experimental parameters, such as receiver gain, rf pulse amplitude and width, etc.

It seems possible to group proposed explanations of the anomaly into two categories: (i) frequency-dependent effects, and (ii) nuclear-spin matrix-element effects, i.e., QSLR. We shall discuss these categories in turn.

The most likely frequency-dependent effect is eddy-current heating, which could play a role in spite of the precautions taken to reduce its effect (Sec. III D). It is hard to see how heating alone, which increases monotonically with frequency and conductivity, could explain the minimum in T_1T observed at $\omega_r/2\pi = 5.5$–6 MHz and the nonmonotonic correlation with residual resistivity shown in Fig. 7. Heating could conceivably give rise to the anomaly in conjunction with some other effect which acted in the opposite direction, and this possibility will be discussed below.

TABLE I. Experimental values of T_1T for In and percent decrease of T_1T per at.% solute, calculated from the data shown in Fig. 6.

Sample	T_1T (msec K)	Percent decrease of T_1T/at.% solute
In	84.8 ± 0.9[a]	...
$In_{0.99}Cd_{0.01}$	81.8 ± 2.2	3.5 ± 2.8[a]
$In_{0.982}Tl_{0.018}$	82.4 ± 1.7	2.8 ± 2.3
$In_{0.99}Sn_{0.01}$	82.5 ± 2.4	2.7 ± 3.0
$In_{0.99}Pb_{0.01}$	82.5 ± 1.3[b]	2.7 ± 1.9

[a] Quoted errors are standard deviations for data from all transitions.

[b] Since no data were available for $r=\frac{5}{2}$, a value of T_1T equal to that for $r=\frac{9}{2}$ was assumed.

If the skin depth in the powder particles is not much greater than the particle diameter, it is possible that an instrumental distortion of the T_1 measurement might occur. This problem has been studied by McLachlan[27] for the much more stringent case of pulsed NMR in metallic single crystals. He concluded that the skin effect does not affect a measurement of T_1 as long as phase-coherent detection is used, as was the case for the present experiments.

There remains the possibility of an actual relaxation mechanism with a frequency dependence in the range 3–8 MHz. This cannot be ruled out experimentally, although it is unlikely on very general grounds. Relaxation by conduction electrons is

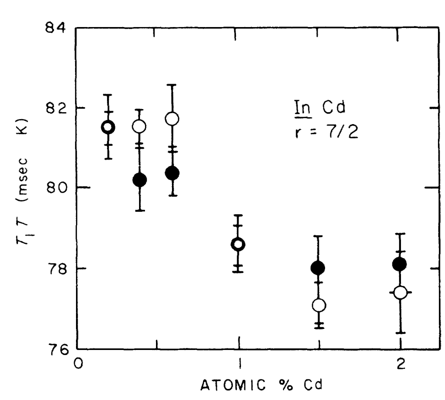

FIG. 8. Dependence of T_1T on Cd concentration for the *In*Cd system. Open and closed circles denote data taken for "short" and "long" saturating pulses, respectively, as in Fig. 6, in this and subsequent figures.

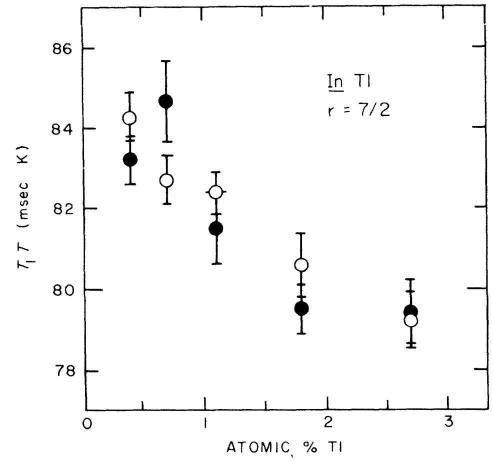

FIG. 9. Dependence of T_1T on Tl concentration for the *In*Tl system.

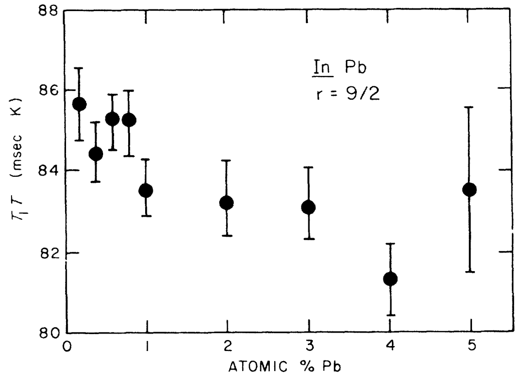

FIG. 11. Dependence of T_1T on Pb concentration for the *In*Pb system.

known to be frequency independent for frequencies less than $\sim E_F/h$, where E_F is the Fermi energy.[15] Paramagnetic impurities, if present, could cause frequency-dependent relaxation, but chemical analysis of the samples used in the present work revealed no paramagnetic trace impurities greater than 10 ppm. These considerations seem to eliminate frequency-dependent effects as sources of the anomaly.

Determination of the amount of QSLR present is, not surprisingly, complicated by its apparent smallness. An analysis of the data based on the perturbation theory of Sec. II F for small admixtures of first- and second-kind QSLR to a dominant MSLR mechanism has been carried out. It will not be presented in detail here, since the result was unphysical in the sense that the data could not be fitted with small positive values W_{Q1} and W_{Q2}. This result makes it unlikely that QSLR alone can be invoked to explain the experimental results. A similar analysis was made for the possibility of combined heating and QSLR effects, again with the result that unphysical values of the parameters involved were needed to fit the data.

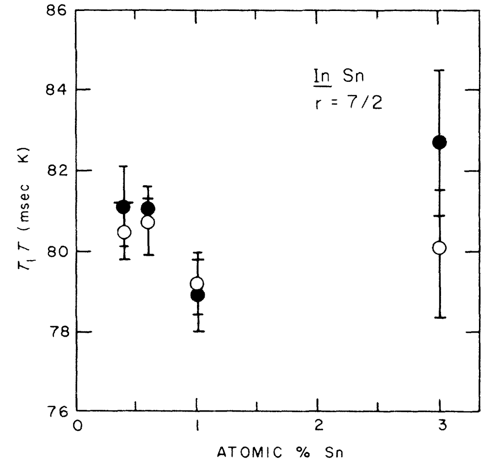

FIG. 10. Dependence of T_1T on Sn concentration for the *In*Sn system.

We are thus unable to advance a hypothesis which explains the observed anomaly. In the absence of a guiding theoretical framework, we shall assume (i) that no QSLR is present, and (ii) that the average of the experimental values for a given sample yields an acceptable value of T_1T. The results obtained in this way are given in Table I.

B. Concentration Dependence of T_1T

Measurements of T_1T were made for a range of solute concentrations and a limited number of transitions, to confirm that the samples selected for the detailed transition-dependence studies discussed above were typical. Concentrations of up to 2-at.% Cd, 2.7-at.% Tl, 4-at.% Sn, and 5-at.% Pb were used. The data, as well as the transitions observed, are given in Figs. 8–11, and show that a monotonic decrease of T_1T with increasing solute concentration is generally observed for all alloy systems investigated. No evidence of extrema in the region 0.5–1-at.% solute can be seen. The rate of decrease T_1T with solute concentration, averaged over the three transitions, is given in Table I for the various solutes. (The quoted standard deviations are dominated by the transition dependence of T_1T.) Although the decrease is not determined very accurately by the data, it seems to be about half as large for Tl solute as for the other three systems.

The absence of extrema in T_1T seems to indicate that the observed minima in the Knight shift[11,12] K are not due to a dependence of the electronic spin susceptibility χ on solute concentration. This can be seen on rather general grounds,[28] since in systems where the generalized complex wave-vector and frequency-dependent susceptibility $\chi(\vec{k}, \vec{k}', \omega)$ varies with system parameters the effect is expected to be observable in both the Knight shift, given by

$$K = \tfrac{16}{3}\pi \langle |u_{\vec{k}}(0)|^2 \chi'(\vec{k}, \vec{k}, \omega_r)\rangle_{\rm av} , \qquad (39)$$

and $(T_1T)^{-1}$, given by[28,29]

$$(T_1T)^{-1} = 2k_B\gamma_n^2 \sum_{\vec{k},\vec{k}'} |u^*_{\vec{k}'}(0)u_{\vec{k}}(0)|^2 \frac{\chi''(\vec{k}, \vec{k}', \omega_r)}{\omega_r} . \qquad (40)$$

Here γ_n is the nuclear gyromagnetic ratio, and $u_{\vec{k}}(0)$ the unperturbed Fermi-surface Bloch function at the nuclear site. The average in Eq. (39) is taken over the Fermi surface. Although the above relations are strictly valid only for the contact interaction in a pure metal, a relation between K and $(T_1T)^{-1}$, via the generalized susceptibility, is expected to exist in an alloy.

This in turn suggests that the minimum in K should be disregarded in comparing the experimental results for K and T_1T. Unfortunately, the behavior of K in the concentration ranges for which T_1T was measured is dominated by the minimum. Practically all that can be said is that to within experimental error K seems to be independent of solute concentration. Thus, it seems that we must abandon the attempt to relate the K and T_1T observations.

There are a number of contributions to the observed T_1T.[24] For our purposes, they may be grouped into two terms:

$$(T_1T)^{-1}_{\rm obs} = (T_1T)^{-1}_{\rm c} + (T_1T)^{-1}_{\rm nc} , \qquad (41)$$

where the subscripts c and nc refer to contact and noncontact terms, respectively. The observed increase in $(T_1T)^{-1}$ could originate in either term. The presence of an exchange interaction between conduction electrons has been shown by Moriya[29] to give rise to an enhancement of $(T_1T)^{-1}_{\rm c}$. The experimental result would be explained if the electron-electron interaction itself increased in the alloys over its value in pure In. Alternatively, $(T_1T)^{-1}_{\rm nc}$ might be enhanced in the alloys. In the absence of a comprehensive theory of solvent nuclear relaxation in dilute alloys, a choice cannot readily be made between these possibilities.

V. CONCLUSION

Precise measurements of spin-lattice relaxation have been carried out in indium metal and dilute In-based alloys using nuclear quadrupole resonance. A small dependence of relaxation time on transition was observed which could not be satisfactorily explained, either under the assumption that a small admixture of quadrupolar relaxation was present, or by the use of several other reasonable mechanisms for a frequency dependence of the observed relaxation time. It was therefore concluded that the observed relaxation is magnetic in origin. Solute concentration dependence of the relaxation exhibited no extremum in the range 0–1-at.% solute, which indicates that the observed minima in the Knight shift[11,12] are not due to a dependence of the electronic susceptibility on solute concentration. A small but discernible decrease in T_1T with increasing solute concentration was observed which could be attributed either to an increase in the electron-electron interaction enhancement of the relaxation rate, or to changes in the noncontact contribution to $(T_1T)^{-1}$.

These results suggest that the relatively large increase with Sn concentration of the *In*Sn electronic specific-heat coefficient observed by White and McCollum[30] is essentially due to electron-phonon enhancement of the electronic density of states, as discussed by these authors. The nuclear spin-lattice relaxation rate is unaffected by this enhancement, since it is cancelled to first order by a corresponding reduction in the hyperfine constant.[31]

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APPENDIX A: EIGENVALUES AND EIGENVECTORS OF THE MAGNETIC RELAXATION MATRICES AND THEIR INVERSES

The ordering of the indices is as exemplified for $I=\frac{5}{2}$:

(i) $I=\frac{5}{2}$: $\lambda_1 = 6W_M$, $\lambda_2 = 20W_M$:

$$\alpha = m \begin{array}{cc} & \overset{\displaystyle i}{\begin{matrix} 1 & \quad 2 \end{matrix}} \\ \begin{matrix} 5/2 \\ \\ 3/2 \end{matrix} & \begin{bmatrix} 2 & 4 \\ & \\ 1 & -5 \end{bmatrix} \end{array} , \quad \alpha^{-1} = i \begin{array}{cc} & \overset{\displaystyle m}{\begin{matrix} 5/2 & \quad 3/2 \end{matrix}} \\ \begin{matrix} 1 \\ \\ 2 \end{matrix} & \begin{bmatrix} \frac{5}{14} & \frac{2}{7} \\ & \\ \frac{1}{14} & -\frac{1}{7} \end{bmatrix} \end{array} ;$$

(ii) $I=\frac{7}{2}$: $\lambda_1 = 6W_M$, $\lambda_2 = 20W_M$, $\lambda_3 = 42W_M$:

$$\alpha = \begin{bmatrix} 3 & -10 & 3 \\ 2 & 5 & -7 \\ 1 & 6 & 7 \end{bmatrix} , \quad \alpha^{-1} = \begin{bmatrix} \frac{1}{6} & \frac{4}{21} & \frac{5}{42} \\ -\frac{1}{22} & \frac{3}{77} & \frac{9}{154} \\ \frac{1}{66} & -\frac{2}{33} & \frac{5}{66} \end{bmatrix} ;$$

(iii) $I=\frac{9}{2}$: $\lambda_1 = 6W_M$, $\lambda_2 = 20W_M$, $\lambda_3 = 42W_M$, $\lambda_4 = 72W_M$:

$$\alpha=\begin{bmatrix}4&-8&14&8\\3&1&-21&-27\\2&4&4&48\\1&3&14&-42\end{bmatrix},\quad \alpha^{-1}=\begin{bmatrix}\frac{1}{11}&\frac{4}{33}&\frac{7}{66}&\frac{2}{33}\\-\frac{9}{143}&\frac{2}{143}&\frac{21}{286}&\frac{9}{286}\\\frac{1}{110}&-\frac{4}{115}&\frac{2}{115}&\frac{4}{115}\\\frac{1}{1430}&-\frac{3}{715}&\frac{7}{715}&-\frac{7}{715}\end{bmatrix}.$$

APPENDIX B: MULTIEXPONENTIAL RELAXATION COEFFICIENTS

The coefficients $b_{ri}=a_{ri}a_i/u_r(0)$ listed below are calculated assuming saturation and observation of a single transition r:

(i) $I=\frac{5}{2}$:

$$b_{ri}=r\;\begin{array}{c|cc|} & \multicolumn{2}{c}{i} \\ & 1 & 2 \\ 5/2 & \frac{3}{7} & \frac{4}{7} \\ 3/2 & \frac{3}{28} & \frac{25}{28} \end{array}\;;$$

(ii) $I=\frac{7}{2}$:

$$b_{ri}=\begin{bmatrix}\frac{3}{14}&\frac{50}{77}&\frac{3}{22}\\\frac{2}{21}&\frac{25}{154}&\frac{49}{66}\\\frac{1}{42}&\frac{18}{77}&\frac{49}{66}\end{bmatrix};$$

(iii) $I=\frac{9}{2}$:

$$b_{ri}=\begin{bmatrix}\frac{4}{33}&\frac{80}{143}&\frac{49}{165}&\frac{16}{715}\\\frac{9}{132}&\frac{5}{572}&\frac{441}{660}&\frac{729}{2860}\\\frac{1}{33}&\frac{20}{143}&\frac{4}{165}&\frac{576}{715}\\\frac{1}{132}&\frac{45}{572}&\frac{49}{165}&\frac{441}{715}\end{bmatrix}.$$

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[19] See, for example, A. R. Edmonds, *Angular Momentum in Quantum Mechanics* (Princeton U. P., Princeton, N. J., 1957).

[20] For $I=\frac{3}{2}$ the relaxation behavior is described by a single exponential with a rate $6W_M+24W_{Q1}+12W_{Q2}$.

[21] A single pulse angle cannot be uniquely defined for NQR in a powdered sample. Only the component of the rf field perpendicular to the crystalline symmetry axis is effective, and this component varies from crystallite to crystallite. It can be shown that a pulse for which the maximum value of θ is 101° maximizes the free-induction signal after the pulse, and that the signal is zero after a pulse of maximum $\theta\approx 208°$. We shall call these pulses $\pi/2$ and π pulses, respectively.

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