

## **Magnetic Spin-Lattice Relaxation in NQR: The $\eta \neq 0$ case.**

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### **ABSTRACT:**

We give solutions for spin-lattice relaxation in NQR due to magnetic interactions, generalized for non-axial crystal fields with  $\eta \neq 0$ . We find analytic expressions for the case  $I = 3/2$ , and give numerical solutions for  $I = 5/2$ ,  $7/2$ , and  $9/2$ . We find that the relaxation curves change considerably with  $\eta$ . Specific results are derived for relaxation due to Fermi contact in metals and other electronic hyperfine interactions. We also describe changes induced by the addition of a magnetic field, indicating fields at which the standard NMR results break down.

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Spin-lattice relaxation in magnetic resonance offers an excellent probe of dynamical effects in solids, as well as electronic charge carriers accessed via the hyperfine interactions. Relaxation times in nuclear quadrupole resonance (NQR) can be utilized in much the same way as in NMR, and these measurements can have great technological importance, for instance in the characterization of polycrystalline metals,<sup>1</sup> incommensurate dielectric<sup>2</sup> and anisotropic metals<sup>3</sup> including the high-temperature superconductors,<sup>4, 5, 6</sup> and dynamics of incommensurate dielectrics.[ref Chen-ailion] For non-axial fields in NQR, however, the energy eigenstates are not identical with magnetic spin states, and the rate equation problem has remained largely unsolved. We address this problem here, giving analytic solutions for the case  $I = 3/2$ , and numerical results for larger spin systems.

The pure quadrupole Hamiltonian can be written,<sup>7</sup>

$$\mathcal{H}_Q = \frac{h\nu_Q}{6} \left( 3 I_z^2 - I(I+1) + \frac{\eta}{2}(I^+ + I^-) \right) \quad \{1\}$$

where spin matrices are represented along the principal axis directions. Here we have defined  $h\nu_Q = \frac{3e^2qQ}{2I(2I+1)}$ , and the electric field gradients (EFG's) are contained in eq and  $\eta$ :  $eq = V_{zz}$ , and  $\eta = \frac{V_{xx} - V_{yy}}{V_{zz}}$ . Conventionally,  $V_{zz}$  has the largest magnitude, and  $V_{xx}$  and  $V_{yy}$  are chosen such that  $0 \leq \eta \leq 1$ . This is not a necessary assumption in what follows, and generally  $\eta$  can assume any value in our results.

We consider first magnetic relaxation by weak fluctuating magnetic fields. The nuclear spin coupling to these fields can be written,

$$\mathcal{H}_M = \alpha I_z + \beta I_x + \gamma I_y, \quad \{2\}$$

where  $\alpha$ ,  $\beta$ , and  $\gamma$  characterize the field strength and anisotropy. (In  $\eta \neq 0$  NQR, we must keep the  $I_z$  as well as  $I_x$  and  $I_y$  terms.) This analysis is appropriate to systems in which electric quadrupole fluctuations can be neglected, such as is often the case for metals. Calculations for quadrupole relaxation in NQR<sup>8-10</sup> have have not been extended to the  $\eta \neq 0$  case.

If we define  $n_i$  as the difference between the population of the  $i^{\text{th}}$  level and its equilibrium value, the rate of change of populations is given by a master equation,

$$\frac{dn_i}{dt} = \sum_{j \neq i} W_{ij} n_j - n_i \sum_{j \neq i} W_{ij}, \quad \{3\}$$

where

$$W_{ij} = \frac{2\pi}{\hbar} |\langle i | \mathcal{H}_M | j \rangle|^2. \quad \{4\}$$

Differences between  $W_{ij}$  and  $W_{ji}$  due to the lattice thermal distribution are accounted for as usual<sup>7</sup> by including equilibrium populations in  $n_i$ . Note that the Andrew-Tunstall<sup>11</sup> result for NMR,  $W_{m,m-1} = W(I + m)(I - m + 1)$ . cannot be used here (this form holds for cylindrical symmetry only, a point that has not always been made clear in the literature. Expression of this problem in terms of fictitious-spin-1/2 operators<sup>12,13</sup> is also difficult since energy states in the present case are not  $I_z$  eigenstates. In general, the  $I_x$  and  $I_y$  matrix elements change with  $\eta$ , and we must keep the  $I_z$  terms in NQR.

For classical fluctuating fields, the rates {4} should be modified to include only the spectral density weighted at the transition frequency.<sup>7</sup> In what follows we assume that the spectral density is independent of the transition frequency (correlation time much larger than  $1/\nu_L$ ). This is appropriate for the high-temperature regime, above the  $T_1$  minimum. (For electron hyperfine interactions, spectral densities will always be very large; a modified rate expression appropriate for electron hyperfine coupling is discussed below.)

States  $i$  and  $j$  are eigenstates of the quadrupole Hamiltonian, {1}; for the case  $\eta = 0$ , these are eigenstates of  $I_z$ , and the resulting spin-lattice recovery curves have been determined for all half-integer spins by MacLaughlin, *et al.*<sup>8</sup> For the general case  $\eta \neq 0$ , we have utilized the symbolic programming system, Mathematica, to find analytic solutions for  $I = 3/2$ , and numerical solutions in the case of other spins.

A convenient representation for the master equations {3} is in matrix form,

$$\frac{dn}{dt} = \mathbf{A} \cdot \mathbf{n}, \quad \{5\}$$

where  $A_{ij} = W_{ij} - \sum W_{ij} \delta_{ij}$  is the  $(2I + 1) \times (2I + 1)$  relaxation matrix. The solution to {5} is a multi-exponential spin-lattice relaxation curve, with exponents given by the eigenvalues of  $\mathbf{A}$ , and coefficients determined from the initial experimental preparation (e.g. saturation of a specified transition). The multiexponential solution described here is a homogeneous relaxation, where multiple exponentials are due to levels that cannot achieve a common spin temperature. The standard method<sup>8, 14, 15</sup> has been to discard the level populations  $n_i$  in favor of population differences between adjacent levels, and to rewrite equation {5} accordingly. For  $\eta \neq 0$  NQR,  $\mathbf{A}$  is not a sparse matrix, and this procedure

becomes non-trivial. We therefore keep the level populations themselves as the quantities of interest. In all cases then, the eigensystem of  $\mathbf{A}$  includes one vector with all equal elements and zero eigenvalue, which is the unchanging total population (always zero in the high-temperature approximation for the traceless Hamiltonian {1}).

**Exact solutions for the  $I = 3/2$  case:**

The normalized eigenstates for the Hamiltonian {1} for  $I = 3/2$  can be written,

$$\begin{aligned}\Psi_1 &= \{-i a, -b, i b, a\}, \\ \Psi_2 &= \{ i a, -b, -i b, a\}, \\ \Psi_3 &= \{ i b, a, i a, b\}, \\ \Psi_4 &= \{-i b, a, -i a, b\},\end{aligned}\quad \{6\}$$

where

$$a = \frac{\sqrt{y-3}}{2\sqrt{3}}, \quad b = \frac{\sqrt{y+3}}{2\sqrt{3}}, \quad \text{and } y = \sqrt{9+3\eta^2}, \quad \{7\}$$

and  $i = \sqrt{-1}$ . The states {6} are in the  $I_z$  basis, defining the  $m = 3/2, 1/2, -1/2,$  and  $-3/2$  states as  $\{1, 0, 0, 0\}, \{0, 1, 0, 0\}, \{0, 0, 1, 0\},$  and  $\{0, 0, 0, 1\},$  respectively. States  $\Psi_1$  and  $\Psi_2$  have energy eigenvalue  $-\frac{h\nu_Q}{6} y,$  and states  $\Psi_3$  and  $\Psi_4$  have eigenvalue  $+\frac{h\nu_Q}{6} y,$  for  $y$  as defined in {7}. Other linear combinations of the degenerate states can be chosen, however we find that the states {6} diagonalize the perturbation {2}, and therefore are most appropriate in this case.

The relaxation matrix  $\mathbf{A}$  can be determined from the spin-state eigensystem {6} and the perturbation {2}. We find that only one of the four eigenmodes of  $\mathbf{A}$  produces population changes observable in NQR. In the energy state basis  $\{\Psi_1, \Psi_2, \Psi_3, \Psi_4\}$  (as opposed to the  $I_z$  basis used above), the observable NQR mode is in all cases  $\{1, 1, -1, -1\},$  and thus removes population from the degenerate states  $(\Psi_3, \Psi_4)$  and adds population to the degenerate states  $(\Psi_1, \Psi_2).$  The spin-lattice relaxation is single-exponential, described by the curve  $\exp[-\rho t],$  where  $\rho$  is the eigenvalue corresponding to the mode described above. We find,

$$\rho = \alpha^2 \frac{2\eta^2}{(3+\eta^2)} + \beta^2 \frac{(3+\eta)^2}{2(3+\eta^2)} + \gamma^2 \frac{(3-\eta)^2}{2(3+\eta^2)}. \quad \{8\}$$

Note that there are no cross terms in {8}, so that correlation of the fluctuations does not modify the results. (We have verified the latter only for  $\alpha, \beta,$  and  $\gamma$  having the same phase, as would be expected for nonmagnetic material with time-reversal symmetry.) Correlation of the fields  $\alpha, \beta,$  and  $\gamma$  could correspond to

fluctuations whose principal axes differ from the EFG principal axes. Such fluctuations can be treated for the  $I = 3/2$  case by taking components ( $\alpha$ ,  $\beta$ , and  $\gamma$ ) resolved into the EFG principal axis system, and inserting these components into {8}.

### Classical isotropic fluctuations:

The relaxation rate {8} simplifies greatly when isotropic magnetic fluctuations are the dominant relaxation process, so that  $\alpha = \beta = \gamma$ . The Hamiltonian {2} can be regarded in this case as  $(\mathbf{I} \cdot \mathbf{H}_{\text{loc}})$ , where  $\mathbf{H}_{\text{loc}}$  is a local field due, for instance, to the untruncated dipolar interaction. The rate {8} then becomes  $\rho = 3 \alpha^2$ , independent of  $\eta$ . This rate is three times the usual definition of  $(T_1)^{-1}$ , or three times the smallest exponent measured in an NMR experiment under the same conditions.

### Fermi Contact Interaction in Metals:

The Fermi Contact Hamiltonian in metals is given by,<sup>7</sup>

$$\mathcal{H}_{\text{FC}} = \frac{8\pi}{3} \delta(r) \gamma_e \gamma_n \hbar^2 \left( I_z S_z + \frac{1}{2}(I^+ S^- + I^- S^+) \right), \quad \{9\}$$

where S operators are for electron spin, and I operators are for nuclear spin. To determine the effective matrix elements for nuclear spin relaxation, we must sum over all electron states:

$$W_{ij} = \frac{2\pi}{\hbar} \sum_{k, \sigma, k', \sigma'} |\langle i | \mathbf{k} \sigma | \mathcal{H}_{\text{FC}} | j \rangle|^2 \delta(\epsilon_{k\sigma} - \epsilon_{k'\sigma'}) f(\epsilon_{k\sigma}) [1 - f(\epsilon_{k'\sigma'})], \quad \{10\}$$

where  $k$  and  $\sigma$  refer to electron orbital and spin states, respectively, and  $f$  is a Fermi function. For nonmagnetic metals we can write the states  $|i \mathbf{k} \sigma\rangle$  as product states,  $|i\rangle |k\rangle |\sigma\rangle$ . The sum over  $k$  states can be performed immediately, giving in the usual way,<sup>7</sup>

$$W_{ij} = W_0 \left\{ 4 |\langle i | I_z | j \rangle|^2 (|\langle + | S_z | + \rangle|^2 + |\langle - | S_z | - \rangle|^2) + |\langle i | I^+ | j \rangle|^2 |\langle - | S^- | + \rangle|^2 + |\langle i | I^- | j \rangle|^2 |\langle + | S^+ | - \rangle|^2 \right\}, \quad \{11\}$$

where  $W_0 = \frac{32 \pi^3}{9} \hbar^3 kT (\gamma_e \gamma_n \rho(\epsilon_F))^2 \langle u(0) \rangle^2$  is equivalent to  $\frac{1}{2T_1}$  in the standard definition (in which  $1/T_1$  is the smallest exponent for NMR relaxation). The electron spin matrix elements are shown explicitly in {11} in terms of the electron spin states  $|+\rangle$  and  $|-\rangle$ . Evaluating these terms yields,

$$\begin{aligned} W_{ij} &= W_0 \left\{ 2 |\langle i | I_z | j \rangle|^2 + |\langle i | I^+ | j \rangle|^2 + |\langle i | I^- | j \rangle|^2 \right\} \\ &= 2W_0 \left\{ |\langle i | I_z | j \rangle|^2 + |\langle i | I_x | j \rangle|^2 + |\langle i | I_y | j \rangle|^2 \right\}. \end{aligned} \quad \{12\}$$

Comparing the result {12} to the definition {2} above, we may define effective field strengths for the Fermi contact interaction,  $\alpha = \beta = \gamma = \sqrt{2W_0}$ , and

use these in {8} to determine the relaxation rate. This equivalence is possible since the final result {8} contains no cross terms, which are excluded from the transition probabilities {12} since separate matrix elements are specified. The result for  $I = 3/2$  is a relaxation rate  $\rho = 6W_0$ . This is independent of  $\eta$ , and is identical to the result found previously<sup>8</sup> for  $\eta = 0$ . Note that this is specific to Fermi contact for  $I = 3/2$ ; elsewhere we demonstrate that a  $T_1$  independent of  $\eta$  is not the general rule.

### Other Hyperfine Interactions in Metals:

Because the core polarization interaction<sup>16</sup> depends upon Fermi contact between s-core states and the nuclei, this interaction will produce transition rates equivalent to {12}, with a prefactor containing the relevant hyperfine coupling constant. It is clear, however, that orbital and dipolar hyperfine couplings in anisotropic metals will cause transition rates that depend in a detailed way on the form of the nuclear eigenstates.

For example, in the case of a dipolar interaction, it is easily shown that for a single orbital at  $\varepsilon_F$  of the form  $Y_1^0$  (quantized about z), the standard form<sup>17</sup> for the dipolar interaction yields transition rates of the form,

$$W_{ij} \propto \{2|\langle i|I_z|j\rangle|^2 + |\langle i|I_x|j\rangle|^2 + |\langle i|I_y|j\rangle|^2\}. \quad \{13\}$$

The resulting relaxation rate for  $I = 3/2$  can be shown from {8} to depend on  $\eta$  as  $\frac{5\eta^2 + 9}{3 + \eta^2}$ . We see therefore that the magnetic relaxation rate measured in NQR depends in a detailed way on the symmetry.

For the case of orbital interactions, where the hyperfine coupling is of the form  $\mathbf{I} \cdot \mathbf{L} = \{I_z L_z + \frac{1}{2}(I^+ L^- + I^- L^+)\}$ , the relaxation rate can be determined directly from {8} if the mixture of orbitals at  $\varepsilon_F$  is known. Unless all m states are equally populated, the spherically symmetric case, the rate will not in general be  $6W_0 = 3/T_1$ . For low-symmetry metals having non-axial EFG's, the orbital mixture will likely involve fewer states than the cubic and hexagonal cases treated by Obata.<sup>17</sup> For instance, in transition-metal one-dimensional conductors with pure  $d_{z^2}$  bands,<sup>18</sup> all  $L^+$  and  $L^-$  matrix elements will be zero, as will the  $L_z$  matrix elements, giving no orbital contribution to the spin-lattice relaxation. However, a mixture of  $m = \pm 1$  orbitals will give a nonzero contribution due to  $L^+$  and  $L^-$  terms. For instance, the addition of a small  $d_{xy} = (Y_2^1 + Y_2^{-1})$  orbital gives a nonzero transition rate proportional to  $|\langle i|\frac{I^+ + I^-}{2}|j\rangle|^2 = |\langle i|I_x|j\rangle|^2$ , so that the  $\beta$  term in {8} determines the relaxation rate. Note that in the orbital case, the crystal field will

mix  $m$  states, so that matrix elements of  $L^+$  and  $L^-$  cannot be treated independently, as could the spin matrix elements above.

### **Numerical results for spins $I > 3/2$ :**

It is not possible to find the analytic solution analogous to {8} for spins  $I > 3/2$  (even utilizing the double-degeneracy for NQR to reduce the spin matrix by one half). Instead, we have solved the eigenstate problem numerically in Mathematica for different values of the asymmetry parameter,  $\eta$ . We developed a programming package so that this can be done for any half-integer spin, keeping all degenerate states. This general approach also allows us to add a static Zeeman field to the problem.

For spins  $5/2$ ,  $7/2$ , and  $9/2$ , magnetic relaxation in NQR is multi-exponential, due to the excitation of more than one eigenmode of the relaxation matrix  $\mathbf{A}$ . The problem of the relative strength of each mode must therefore be addressed by expanding the initial population differences,  $\mathbf{n}_0$ , in terms of the eigenvectors of  $\mathbf{A}$ . We have calculated  $\mathbf{A}$  numerically by first calculating the energy eigenvalues (in the  $I_z$  representation). Equilibrium energy-state populations were equated to the state energies, in a high-temperature approximation. For a transition between two pairs of degenerate energy states, we interchanged the populations of the states, and subtracted the equilibrium populations to find the initial population differences,  $\mathbf{n}_0$ . Thus for a transition between states  $(\Psi_1, \Psi_2)$  and states  $(\Psi_3, \Psi_4)$  for spin  $I = 5/2$ , the initial vector is  $\mathbf{n}_0 = \{\delta E, \delta E, -\delta E, -\delta E, 0, 0\}$ , where  $\delta E = (E_3 - E_1)$ . If  $\mathbf{C}$  is the matrix whose columns are normalized normal modes of  $\mathbf{A}$  (consistent with Narath's<sup>15</sup> notation),  $\mathbf{n}_0$  in the normal mode basis is equal to  $\mathbf{C}^{-1} \cdot \mathbf{n}_0$ , where  $\mathbf{C}^{-1}$  is the inverse of  $\mathbf{C}$ , or its transpose in this case. The relaxation curve is then given by the sum  $\sum (\mathbf{C}^{-1} \cdot \mathbf{n}_0)_i \exp(-\rho_i t)$ , where  $i$  counts through eigenvectors of  $\mathbf{A}$ ,  $(\mathbf{C}^{-1} \cdot \mathbf{n}_0)_i$  is an element of the vector, and  $\rho_i$  is the corresponding eigenvalue.

For the case  $\eta = 0$ , eigenvalues  $\rho_i$  are given by<sup>8</sup>  $(6W_0, 20W_0)$  for  $I = 5/2$ ,  $(6W_0, 20W_0, 42W_0)$  for  $I = 7/2$ , and  $(6W_0, 20W_0, 42W_0, 72W_0)$  for  $I = 9/2$ , where  $2W_0$  is equal to  $1/T_1$  as usually defined. These NQR eigenvalues correspond to eigenmodes of  $\mathbf{A}$  that have even symmetry under coordinate reversal, whereas the modes observable in NMR have odd symmetry. For  $\eta \neq 0$ , with no Zeeman field, the symmetry is unchanged, so that the number of modes for NQR relaxation is restricted to 2, 3, and 4 for  $I = 5/2$ ,  $7/2$ , and  $9/2$ , respectively.

We have calculated relaxation exponents and coefficients specifically for the case of Fermi contact relaxation, for which the matrix elements have been

determined above. The methods described here, however, will work for any asymmetric magnetic interaction. We give results for Fermi contact in terms of  $W_0$  as defined above, where  $2W_0$  is the smallest rate observable in NMR. As before, these results apply to isotropic fluctuations above the  $T_1$  minimum, with a suitable scaling of  $W_0$ . Results are given in figures 1-6. The rates change with  $\eta$  in nearly the same way for each spin, but they are not identical. Note that these rates are not constant, as they were for  $I = 3/2$ . However, our results show that for the contact interaction, the smallest term is exactly  $6W_0$  in all cases, which for the  $I = 3/2$  case was the only exponent observed. In the general case of anisotropic fluctuations, this smallest term also changes with  $\eta$ .

Therefore, if the relaxation is of the contact type, we demonstrate that the long-time tail of the relaxation curve can be fit to the exponent  $6W_0$ , independent of the details of the EFG tensor. This result may be particularly useful to characterize disordered metals, in which  $\eta$  can be distributed inhomogeneously. However, the full relaxation curve, with coefficients and rates given in figures 1-6, contains detailed information that can be used to verify the relaxation mechanism. In particular, we have used the numerical method described here for anisotropic interactions, which provides a promising means to characterize hyperfine fields in metals.

#### **Addition of a Magnetic field:**

With the addition of a static magnetic field, the energy eigenstates become equivalent to pure  $I_z$  states in the high field limit. We address the approach of magnetic spin-lattice relaxation curves to the high-field limit by using the numerical methods described above. This can be done by adding a Zeeman term to the Hamiltonian {1}, and determining the eigensystem of the resulting Hamiltonian. The relaxation matrix  $\mathbf{A}$  can therefore be determined, and from its eigenmodes the relaxation curves are calculated as above. The Zeeman field destroys the inversion symmetry of the Hamiltonian, and as a result all eigenmodes contribute to the observed relaxation curve (*e. g.* nine exponentials in general for  $I = 9/2$ ).

In figure 7 are shown exponents calculated for  $I = 9/2$ , for the addition of a Zeeman Hamiltonian  $\mathcal{H}_Z = h\nu_L I_z$ , corresponding to a magnetic field along the z EFG principal axis and a Larmor frequency  $\nu_L = \frac{\gamma H_0}{2\pi}$ . These curves were calculated specifically for a contact interaction, as in figures 1-6, and for a fixed orientation of the EFG's, with  $\eta = 1$ . The energies for this situation are shown in

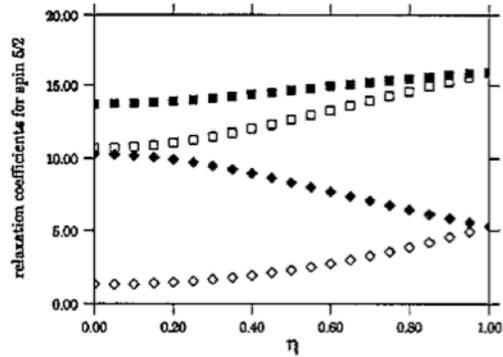
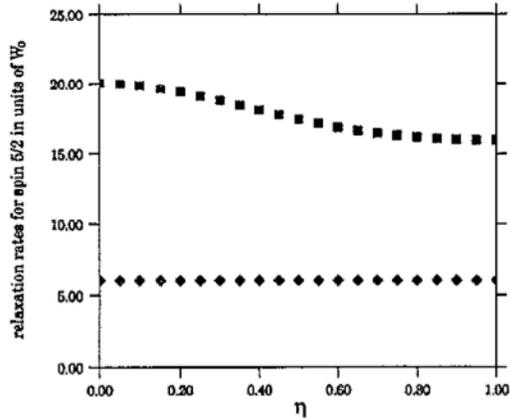
figure 8. Prominent peaks and changes in the rates in figure 7 can be identified with energy-level anti-crossings. Clearly, in these regions the eigenstates become strongly mixed, thereby modifying the relaxation matrix  $\mathbf{A}$ . Note that more than one rate is affected strongly by each level crossing since the eigenmodes of  $\mathbf{A}$  are mixtures of energy states. The spin-lattice relaxation for all transitions thus exhibits this structure, including transitions between higher-energy states whose energies change smoothly over the entire range. Changes with field becomes smaller as  $\eta$  approaches zero, until finally level anti-crossings will vanish for  $\eta = 0$ . For the non-axial case, however, the rates approach the high-field limit only above the highest-field anti-crossing, or above a maximum Larmor frequency of approximately  $\nu_Q$ ,  $2\nu_Q$ ,  $3\nu_Q$  and  $4\nu_Q$ , for  $I = 3/2$ ,  $5/2$ ,  $7/2$ , and  $9/2$  respectively. Thus we demonstrate explicitly the magnetic fields for which standard NMR results can be utilized in  $\eta \neq 0$  quadrupole systems.

## References:

1. J. Abart, *et al.*, J. Chem. Phys. **78**, 5468 (1983).
2. S. Chen and D. C. Ailion, Solid State Commun. **69**, 1041 (1989).
3. B. H. Suits and C. P. Slichter, Phys. Rev. B **29**, 41 (1984).
4. C. H. Pennington, *et al.*, Phys. Rev. B **39**, 2902 (1989).
5. R. E. Walstedt, *et al.*, Phys. Rev. B **40**, 2572 (1989).
6. H. Monien, D. Pines and C. P. Slichter, Phys. Rev. B **41**, 11 120 (1990).
7. Charles P. Slichter, *Principles of Magnetic Resonance* (Springer-Verlag, Berlin, 1980).
8. D. E. MacLaughlin, J. D. Williamson and J. Butterworth, Phys. Rev. B **4**, 60 (1971).
9. M. Gordon and M. J. R. Hoch, J. Phys. C: Solid State Phys. **11**, 783 (1978)
10. T. Rega, J. Phys.: Condens. Matter **3**, 1871 (1991).
11. E. R. Andrew and D. P. Tunstall, Proc. Phys. Soc. **78**, 1 (1961).
12. Shimon Vega, J. Chem. Phys. **68**, 5518 (1978).
13. D. Petit and J.-P. Korb, Phys. Rev. B **37**, 5761 (1988).
14. W. W. Simmons, W. J. O'Sullivan and W. A. Robinson, Phys. Rev. **127**, 1168 (1962).
15. Albert Narath, Phys. Rev. **262**, 320 (1967).
16. Y. Yafet and V. Jaccarino, Phys. Rev. **133**, 1630 (1964).
17. Y. Obata, J. Phys. Soc. Japan **18**, 1020 (1963).
18. E. Canadell, *et al.*, Inorg. Chem. **29**, 1401 (1990).

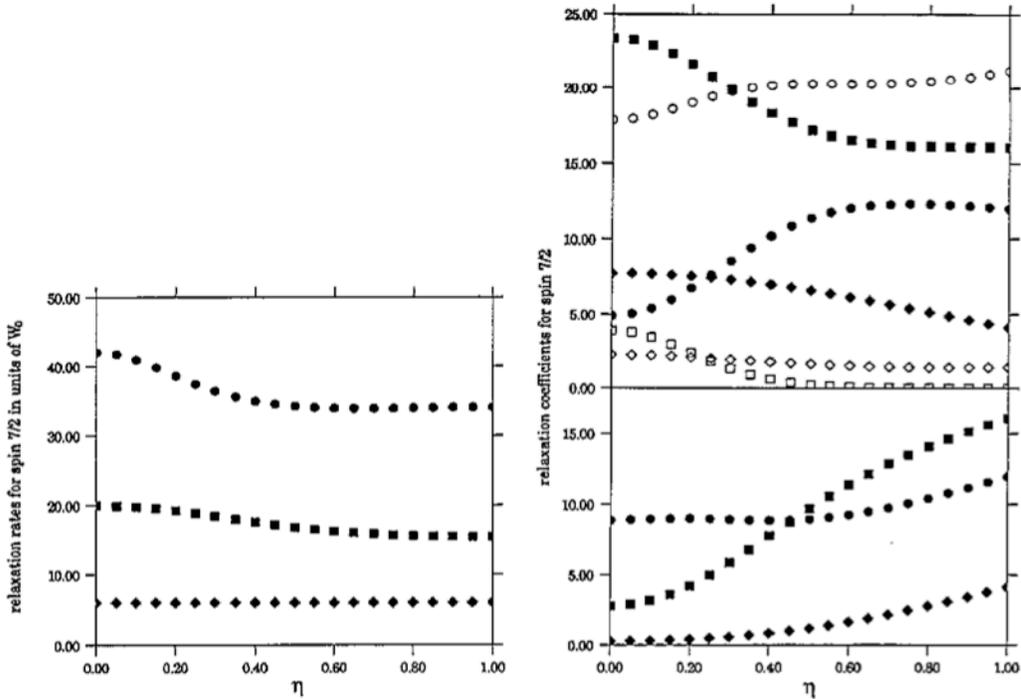
**Figure 1** (left): Relaxation rates vs.  $\eta$  for spin 5/2, in units of  $W_0$  (defined in the text), for Fermi contact interaction.

**Figure 2** (right): Exponential coefficients for spin 5/2 as a function of  $\eta$ . The '5/2-3/2' and the '3/2-1/2' transitions are represented by filled and open symbols, respectively. The symbols correspond to those with the same shape used for the rates in figure 1. Coefficient scaling is described in the text.



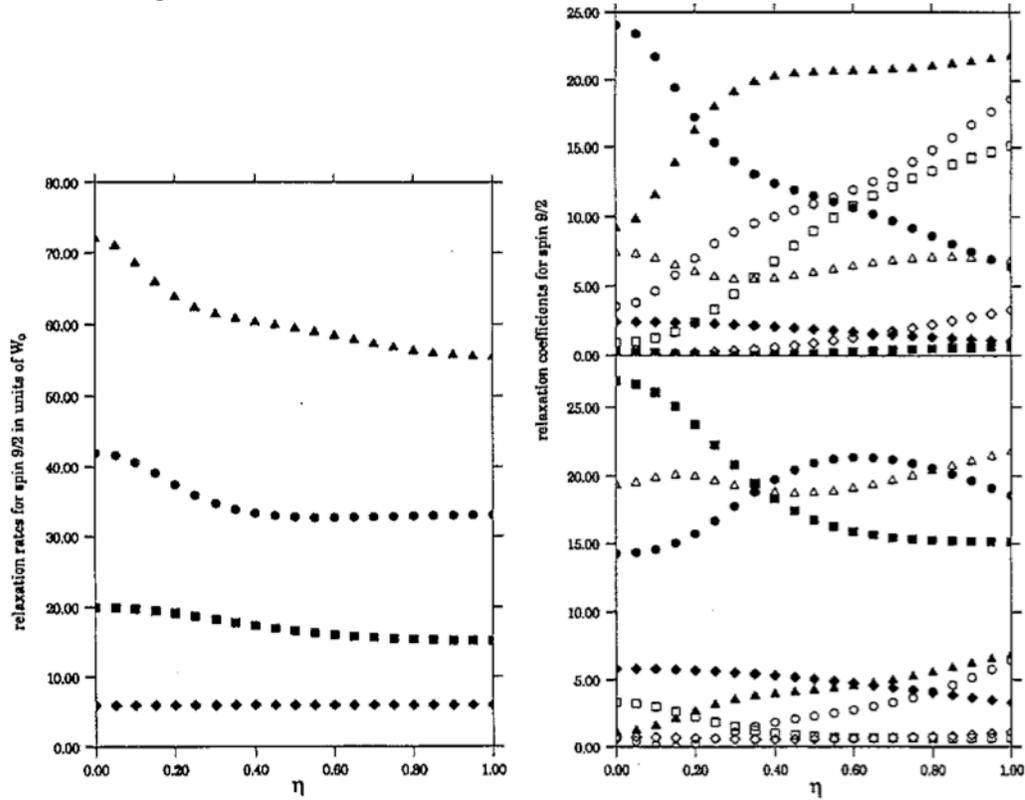
**Figure 3** (left): Relaxation rates vs.  $\eta$  for spin 7/2, in units of  $W_0$  (defined in the text), for Fermi contact interaction.

**Figure 4** (right): Exponential coefficients for spin 7/2 as a function of  $\eta$ . The upper portion of the figure shows the '7/2-5/2' and the '5/2-3/2' transition coefficients using filled and open symbols, respectively. The lower portion contains the '3/2-1/2' transition coefficients. The symbols correspond to those with the same shape used for the rates in figure 3. Coefficient scaling is described in the text.



**Figure 5** (left): Relaxation rates vs.  $\eta$  for spin 9/2, in units of  $W_0$  (defined in the text), for Fermi contact interaction.

**Figure 6** (right): Exponential coefficients for spin 9/2 as a function of  $\eta$ . The upper portion of the figure shows the '7/2-5/2' and the '3/2-1/2' transition coefficients using filled and open symbols, respectively. The '9/2-7/2' and the '5/2-3/2' transition coefficients are in the lower portion, shown using filled and open symbols, respectively. The symbols correspond to those with the same shape used for the rates in figure 5 for the relaxation rates. Coefficient scaling is described in the text.



**Figure 7** (left): Dependence of the relaxation rates upon a magnetic field along the quadrupolar  $z$  symmetry axis for spin  $9/2$  and  $\eta = 1$ . Relaxation is via Fermi contact interaction. Rates have units of  $W_0$  (defined in the text).

**Figure 8** (right): Energy states of a spin  $9/2$  nucleus in a completely antisymmetric ( $\eta = 1$ ) quadrupolar field as a function of an applied magnetic field along the  $z$  symmetry axis.

