Second-Order Quadrupolar Echo in Solids

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Echoes have been observed in an NMR experiment on isolated ^{11}B nuclei in a Si matrix which arise from a refocusing of the second-order quadrupolar interaction. The quadrupolar couplings are so large that only the central transition is excited. A theoretical treatment using fictitious spin-$\frac{1}{2}$ operators is presented which shows that the fictitious secular part of the interaction is responsible for the echo formation. The decay of the echo train is caused by the fictitious nonsecular terms.

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The Zeeman eigenstates in high-field NMR can be perturbed significantly by the quadrupolar interaction (QI). For half-integer nuclei, the energy gap corresponding to the central transition ($m=\frac{1}{2}\leftrightarrow m=-\frac{1}{2}$) is not affected by the QI in first order [1,2]. When the QI is sufficiently small, an rf pulse can still excite all transitions between Zeeman levels. The satellite lines covered by the receiver dead time can be recovered by the application of a second pulse during or immediately after the free-induction decay (FID), which generates quadrupolar echoes [3,4]. However, when the QI is so large that only the central transition is excited, second-order effects of the QI must be considered. MAS (magic-angle spinning) partially reduces the second-order quadrupolar broadening on the central transition [5]. DAS (dynamic-angle spinning) may eliminate the second-order effect but its applicability is limited by the spinning rate of the rotor [6].

We have observed an echo of the ^{11}B resonance in B-doped Si which is due to a refocusing of the second-order QI on the central transition. Echoes of this type have been observed before [4,7–13]. In most cases they were reported to occur in slightly distorted cubic crystals in which dipolar couplings between both like and unlike nuclei are present [4,8,11]. Inhomogeneous broadening originating from heteronuclear dipolar interactions were thought to be responsible for the echo formation [7,8]. In our sample, dipolar interactions are negligible. Furthermore, the QI is so strong that only the central transition is excited by the rf pulses.

Accordingly, we express the QI in terms of the fictitious spin-$\frac{1}{2}$ operators (FSO) [14] and use time-independent perturbation theory. FSO's are more suitable than the total angular momentum operators for calculating the magnetization resulting from the detection of only the central transition. In fact, FSO's must be used if only a subset of the available energy levels is excited and detected.

The QI Hamiltonian in the laboratory frame is given by [2,8]

$$H_Q=\tfrac{1}{4}\omega_Q a_0\{I_z^2-\tfrac{1}{3}I(I+1)\}+\tfrac{1}{6}\omega_Q\{a_{1+}(I_zI_++I_+I_z)+a_{1-}(I_-I_z+I_zI_-)+a_{2+}I_+^2+a_{2-}I_-^2\}\,, \tag{1}$$

where $\omega_Q=3e^2qQ/2I(2I-1)$, and the various a_i denote angular factors which depend on the orientation of the principal axes of the electric-field gradient in the laboratory frame. Utilizing time-independent perturbation theory, Eq. (1) can be converted to a matrix representation whose elements V_{mn} between Zeeman eigenstates are given by

$$V_{mn}=\langle m|H_Q|n\rangle+\sum_{p\neq n}\frac{\langle m|H_Q|p\rangle\langle p|H_Q|n\rangle}{(\varepsilon_n-\varepsilon_p)}\delta_{mn}+{\sum_{q\neq(m,n)}}'\frac{\langle m|H_Q|q\rangle\langle q|H_Q|q\rangle\langle q|H_Q|n\rangle}{(\varepsilon_m-\varepsilon_q)(\varepsilon_n-\varepsilon_q)}\,, \tag{2}$$

where the prime in the final term denotes the restriction $m\neq n$.

The first term yields the first-order correction of the eigenvalues for $m=n$, or causes direct transitions for $m\neq n$. The second term represents the second-order correction of the eigenvalues determined by the fictitious secular part. The third term in Eq. (2) describes indirect transitions between the states $|m\rangle$ and $|n\rangle$ through intermediate states $|q\rangle$, which become important when direct transitions via the perturbing Hamiltonian are forbidden. The quadrupolar Hamiltonian can then be expressed in terms of FSO resulting in a linearization of the various operator-product terms.

The nonsecular terms contribute to the correction of eigenvalues starting from second order and can cause direct transitions between the different eigenstates, except the central transition which has nonzero matrix element only via the indirect route. The second-order correction of the eigenvalues by the nonsecular parts can be written as a sum of $\omega_Q^{(2)}I_z^{23}$ and $\omega_Q^{(2)'}I_z^{14}$, where 1 through 4 correspond to the magnetic quantum numbers $\frac{3}{2}$ through $-\frac{3}{2}$ [15]. $\omega_Q^{(2)}$ and $\omega_Q^{(2)'}$ depend on the orientation of the electric-field gradients. Transitions between the Zeeman eigenstates caused by QI can be expressed as the sum of $\Delta_\alpha^{ij}I_\alpha^{ij}$ and $\delta_\alpha^{23}I_\alpha^{23}$, where α can be either x or y and (ij)

denotes any combination from 1 through 4 except a (23) combination. As can be seen from Eq. (2), $\delta_\alpha^{23}/\Delta_\alpha^{ij}$ is of the order of $(\omega_Q/\omega_0)^2$.

All the physical quantities in terms of the FSO relevant to this problem are summarized for spin $\frac{3}{2}$ as follows:

$$\rho_0 = kI_z = k(3I_z^{14} + I_z^{23}),$$

$$H_Z = -\omega_0 I_z = -\omega_0(3I_z^{14} + I_z^{23}),$$

$$H_Q = H_Q^{\text{sec}} + H_Q^{\text{nonsec}} = H_Q^{\text{sec}} + H_{Q(\text{fic})}^{\text{sec}} + H_{Q(\text{fic})}^{\text{nonsec}}$$

$$= \frac{\omega_Q}{2}(I_z^{12} - I_z^{34})a_0(\theta,\phi) + \{\omega_Q^{(2)} I_z^{23} - \omega_Q^{(2)'} I_z^{14}\} + \sum_\alpha \left\{ \delta_\alpha^{23} I_\alpha^{23} + \sum_{i<j}{}' \Delta_\alpha^{ij} I_\alpha^{ij} \right\},$$

$$H_{\text{rf}} = -\omega_1 I_x = -\omega_1(\sqrt{3}I_x^{12} + 2I_x^{23} + \sqrt{3}I_x^{34}).$$

In this notation, the first term in Eq. (2) causes the direct transitions $\Delta_\alpha^{ij} I_\alpha^{ij}$ for $m \neq n$. The third term contributes indirect transitions denoted by $\delta_\alpha^{23} I_\alpha^{23}$.

Since the central transition is not affected by the secular part of the QI, it can be removed by going into a reduced representation defined as

$$\rho_{\text{red}}(t) = \exp(iH_Q^{\text{sec}} t)\rho(t)\exp(-iH_Q^{\text{sec}} t).$$

Only the central transition is excited if the conditions $\omega_0 \gg \omega_Q \gg \omega_1 \gg \omega_Q^{(2)}, \omega_Q^{(2)'}$ are satisfied experimentally. Therefore it suffices to consider a reduced density operator $\rho_{\text{red}}^{23}(t)$, which is a linear combination of I_α^{23} and obeys the Liouville–von Neumann equation

$$i\frac{d\rho_{\text{red}}^{23}(t)}{dt} = [H_{\text{red}}^{23} + H_{Q(\text{fic})}^{\text{nonsec}}(t), \rho_{\text{red}}^{23}(t)], \tag{3}$$

with

$$H_{\text{red}}^{23} = -\omega_0 I_z^{23} + \omega_Q^{(2)} I_z^{23} + \delta_x^{23} I_x^{23} + \delta_y^{23} I_y^{23},$$

$$H_{Q(\text{fic})}^{\text{nonsec}}(t) = \exp(iH_Q^{\text{sec}} t)\left\{ \sum_\alpha \sum_{i<j}{}' \Delta_\alpha^{ij} I_\alpha^{ij} \right\}(\text{H.c.}), \tag{4}$$

where the various parameters in Eq. (4) can be obtained from Eqs. (1) and (2) as

$$\omega_Q^{(2)} = (\omega_Q^2/3\omega_0)(2a_{1+}a_{1-} - a_{2+}a_{2-}), \tag{5a}$$

$$\delta_x^{23} = (\omega_Q^3/6\omega_0^2)\text{Re}(a_0 a_{1-} a_{2+}), \tag{5b}$$

$$\delta_y^{23} = -(\omega_Q^3/6\omega_0^2)\text{Im}(a_0 a_{1-} a_{2+}), \tag{5c}$$

and (H.c.) denotes the Hermitian conjugate of the time-development operator. Notice that $H_{Q(\text{fic})}^{\text{nonsec}}(t)$ does not contain the term $\delta_\alpha^{23} I_\alpha^{23}$ and so it differs from $H_{Q(\text{fic})}^{\text{nonsec}}$.

Even though the magnitude of $H_{Q(\text{fic})}^{\text{nonsec}}(t)$ is much larger than $\delta_x^{23} I_x^{23} + \delta_y^{23} I_y^{23}$, the time-dependent terms are not effective in changing the coherence of the central transition because of their rapid oscillations [16]. So Eq. (3) is further simplified to

$$i\frac{d\rho_{\text{red}}^{23}(t)}{dt} = [H_{\text{red}}^{23}, \rho_{\text{red}}^{23}(t)]. \tag{6}$$

During a short rf pulse on resonance with the central transition the broadening effect of the second-order QI on the central transition can be neglected with the condition $\omega_1 \gg \omega_Q^{(2)}$. The density operator is then given by $-kI_y^{23}$ after a 90_x° pulse. A 90° pulse is defined as one rotating the magnetization of the effective spin-$\frac{1}{2}$ system through 90°. It can be seen from Eqs. (5a)–(5c) that δ_α^{23} is smaller than $\omega_Q^{(2)}$ by an order of ω_Q/ω_0.

The effect of the fictitious nonsecular term on the transverse magnetization can be examined by taking a coordinate transformation

$$\rho^*(t) = \exp\{i(-\omega_0 + \omega_Q^{(2)})I_z^{23} t\}\rho_{\text{red}}^{23}(t)(\text{H.c.}).$$

The coordinate transformation leading to $\rho^*(t)$ is introducing an interaction representation with respect to both Zeeman precession and the second-order quadrupolar broadening. It thus differs from the rotating-frame transformation which is an interaction representation with respect to the Zeeman interaction only.

Then the Liouville equation for $\rho^*(t)$ becomes

$$i\frac{d\rho^*(t)}{dt} = \exp\{i(-\omega_0 + \omega_Q^{(2)})I_z^{23} t\} \times [\delta_x^{23} I_x^{23} + \delta_y^{23} I_y^{23}, \rho_{\text{red}}^{23}(t)](\text{H.c.}). \tag{7}$$

In general, $\rho_{\text{red}}^{23}(t)$ can be decomposed into two components, viz. longitudinal and transverse components. As can be seen from Eq. (7), a transverse coherence is converted to a longitudinal coherence very effectively, whereas the longitudinal coherence I_z^{23} is not affected significantly by the fictitious nonsecular terms because of their rapid oscillation. In other words, the commutator $[\delta_x^{23} I_x^{23}, -kI_y^{23}]$ creates a I_z^{23} term that is invariant under $\exp\{i(-\omega_0 + \omega_Q^{(2)})I_z^{23} t\}$. In contrast, the action of the fictitious nonsecular term on I_z^{23}, $[\delta_x^{23} I_x^{23}, k' I_z^{23}]$, creates an I_y^{23} term that oscillates rapidly under $\exp\{i(-\omega_0 + \omega_Q^{(2)})I_z^{23} t\}$, and therefore has no influence. This results in an irreversible loss of the transverse to longitudinal coherence by the fictitious nonsecular term.

With an initial density operator $-kI_y^{23}$ after a 90_x° pulse, integration of Eq. (7) leads to, up to first order in δ_α^{23},

$$\rho^*(t) = -kI_y^{23} - k(t - t_0)\delta_x^{23} I_z^{23}, \tag{8}$$

where the second term denotes the irreversible loss of the transverse coherence. The smaller $t - t_0$, the more accurate is Eq. (8). If one is only interested in the decay of transverse magnetization, then Eq. (8) can be stated, for all practical purposes, as

$$I_y^{23}(t - t_0) = I_y^{23}(t_0)\exp\{-|\delta_x^{23}|(t - t_0)\}, \tag{9}$$

with $t - t_0 \ll T_1$.

The loss of the transverse coherence can be viewed as follows: The rf pulse sets up a transverse coherence whose quantum state is a linear combination of the $|2\rangle$ and $|3\rangle$ states with equal probability amplitude. The fictitious nonsecular terms, $\delta_x^{23}I_x^{23}+\delta_y^{23}I_y^{23}$, then induce transitions to states with a definite magnetic quantum number and, as a result, establish a spin temperature within the spin system. This irreversible loss of transverse magnetization does not require heat exchange with the lattice and proceeds in a time $\ll T_1$. Although the nonsecular terms are described in terms of the operators I_α^{23}, they arise from indirect transitions given by the third term of Eq. (2). So, while the fictitious secular terms, which include a variation of the static electric-field gradients, dephase the macroscopic transverse coherence reversibly, the nonsecular terms destroy the coherence both macroscopically and locally. Therefore they reduce the observed magnetization of the effective spin-$\frac{1}{2}$ system irreversibly.

The density operator in the rotating frame at time t_1 after the application of the 90°_x pulse is obtained from Eqs. (6) and (9),

$$\rho_R(t_1)=\exp(-i\omega_Q^{(2)}t_1I_z^{23})\{-kI_y^{23}\exp(-|\delta_x^{23}|t_1)\}(\text{H.c.})\,.$$

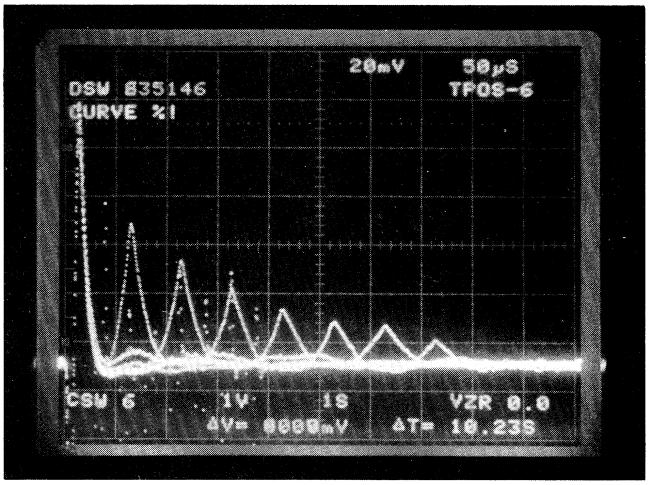

FIG. 1. Second-order quadrupolar echoes in Si(B) generated by 90°_x-t_1-180°_y pulse sequences. Sweep: 50 μs/div. The pulse separation was varied from 25–175 μs in steps of 25 μs. The 180°_y pulses appear as dotted vertical lines.

In general, each individual spin has different $\omega_Q^{(2)}$ depending on the magnitude and orientation of the electric-field gradient at the position of the nucleus. Spins with different $\omega_Q^{(2)}$ will dephase in a similar fashion as spins in an inhomogeneous magnetic field since both Hamiltonians have the same form. It then follows that a second 180° pulse can refocus the dephasing caused by $\omega_Q^{(2)}I_z^{23}$ in a fashion similar to the Hahn spin echo. The density operator at time t_2 after a 180°_y pulse is then given by

$$\begin{aligned}\rho_R(t_2)&=\exp(-i\omega_Q^{(2)}t_2I_z^{23})\exp(-|\delta_x^{23}|t_2)\exp(-i\pi I_y^{23})\rho_R(t_1)(\text{H.c.})\\&=\exp\{-i\omega_Q^{(2)}(t_2-t_1)I_z^{23}\}\{-kI_y^{23}\exp[-|\delta_x^{23}|(t_1+t_2)]\}(\text{H.c.})\,.\end{aligned}\tag{10}$$

The echo will form at a time after the second pulse equal to the pulse separation. It should be noted that the second-order quadrupolar echo increases uniformly with the length of the second pulse, reaching its maximum for a pulse length corresponding to a 180° pulse. It can be verified that the application of a 180°_x pulse generates an inverted, but otherwise identical, echo.

The sample is made from Czochralski-grown B-doped Si wafers [17] with a (111) surface orientation and 0.5 mm thickness. The concentration of B in Si is $2.2\times10^{20}/\text{cm}^3$, i.e., ruling out clustering, there is, on the average, one B atom at every six lattice sites. Four square-shaped pieces are stacked and glued together. The area of each piece is about 8 mm×8 mm.

Figure 1 shows an experimental verification of Eq. (10). The data were taken at 30 MHz and 4.2 K. FID and echoes are characterized by a T_2^* which is a measure of the dephasing of the transverse magnetization as a consequence of the inhomogeneous broadening caused by the second-order QI. The measured value of T_2^* is 16 μs which corresponds to $\omega_Q^{(2)}/\gamma\approx7.3$ G. Second-order quadrupolar echoes were obtained with pulse separations of up to 175 μs. It is certainly possible to generate echoes for still longer pulse separations. The decay of the echo train is roughly exponential with a time constant of 340 μs, which is a measure of $|\delta_x^{23}|^{-1}$. A ratio of $|\delta_x^{23}/\omega_Q^{(2)}|\approx1/20$ appears to be reasonable for our sample [18]. Further experimental data will be published elsewhere.

This interpretation of the echo formation in the presence of a strong quadrupolar coupling is believed to be applicable to any solid containing half-integer nuclei. Of course, both theory and data analysis will be more complex if internuclear dipolar couplings cannot be neglected [13]. Since the dipolar interaction is not refocused by a 90°-180° pulse sequence, its presence results in a faster decay of the echo peaks than in the case where only the QI exists [18]. In our sample, contrary to previous experiments [7–11], the quadrupolar interaction is so strong that even in second order it is still larger than the dipolar coupling between the widely dispersed B atoms. It would be interesting to see whether the decay of echo train can be reduced by sample spinning along the z axis. If so, high-resolution NMR of the quadrupolar broadened lines could be vastly improved.

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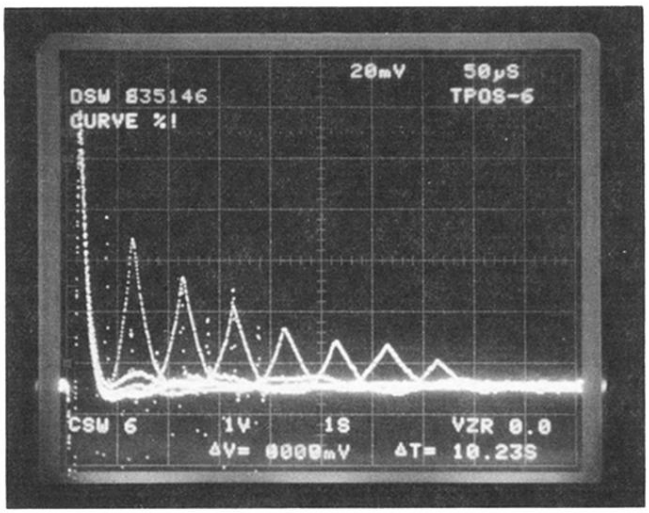
[1] R. V. Pound, Phys. Rev. **79**, 685 (1950).
[2] M. H. Cohen and F. Reif, in *Solid State Physics,* edited by F. Seitz and D. Turnbull (Academic, New York, 1957), Vol. 5, p. 321.
[3] I. Solomon, Phys. Rev. **110**, 61 (1958).
[4] W. W. Warren and R. E. Norberg, Phys. Rev. **154**, 277 (1967).
[5] H. J. Jakobsen, J. Skibsted, H. Bildsøe, and N. C. Nielsen, J. Magn. Reson. **85**, 173 (1989).
[6] K. T. Mueller, B. Q. Sun, G. C. Chingas, J. W. Zwanziger, T. Terao, and A. Pines, J. Magn. Reson. **86**, 470 (1990).
[7] J. Butterworth, J. Proc. Phys. Soc. London **86**, 297 (1965).
[8] O. Kanert and M. Mehring, in *NMR,* edited by P. Diehl, E. Fluck, and R. Kosfeld (Springer, Berlin, 1971), Vol. 3, p. 1. This article reviews the work related to the QI up to 1969.
[9] K. R. Jeffrey, J. Chem. Phys. **66**, 4677 (1977).
[10] E. Oldfield and R. J. Kirkpatrick, Science **227**, 1537 (1985).
[11] T. K. Halstead, P. A. Osment, B. C. Sanctuary, J. Tegenfeldt, and I. J. Lowe, J. Magn. Reson. **67**, 267 (1986).
[12] J. Haase and H. Pfeifer, J. Magn. Reson. **86**, 217 (1990).
[13] J. Haase, H. Pfeifer, and E. Oldfield (private communication).
[14] A. Wokaun and R. R. Ernst, J. Chem. Phys. **67**, 1752 (1977).
[15] S. Vega and Y. Naor, J. Chem. Phys. **75**, 75 (1981).
[16] A. Abragam, *The Principles of Nuclear Magnetism* (Oxford, London, 1961), Chap. IV.
[17] C. W. Pearce, in *VLSI Technology,* edited by S. M. Sze (McGraw-Hill, New York, 1983), Chap. I.
[18] D. Y. Han, Ph.D. thesis, University of North Carolina at Chapel Hill, 1990 (unpublished).



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