Comment on "Second-Order Quadrupolar Echo in Solids"

In a recent Letter, Han and Kessemeier [1] report observations of NMR spin echoes of boron impurities in silicon, and identify echo relaxation with a mechanism due to nonsecular terms in the Zeeman–electric-quadrupole Hamiltonian. I argue that spin relaxation of this type cannot be caused by a static electric quadrupole interaction, and must in this case be due to dipolar interactions or to fluctuating hyperfine fields.

In this problem, a distinction must be made between eigenstates of the Zeeman plus quadrupole Hamiltonians (H_Z+H_Q), and eigenstates of the pure Zeeman Hamiltonian. The former, Zeeman-quadrupole states, will be denoted Ψ_m^{ZQ}, whereas the latter states, Ψ_m^0, are the familiar I_z spin eigenstates. A coherence between states Ψ_m^{ZQ} is a sum of eigenstates with a well-defined phase relationship (or a statistically dominant phasing). A "90° pulse" will establish such a coherence in quadrupole NMR, and the static Zeeman-quadrupole field will induce a linear advance of the coherence phase, equivalent to spin precession. The static Zeeman-quadrupole field cannot, however, induce relaxation, since the states are eigenstates.

Consider, then, the Hamiltonian for the quadrupole interaction:

$$\langle\Psi_n^0|H_Q|\Psi_m^0\rangle=\langle\Psi_n^0|\tfrac{1}{4}\omega_Q a_0\{I_z^2-\tfrac{1}{3}I(I+1)\}$$
$$+\tfrac{1}{6}\omega_Q\{a_{1+}(I_zI_++I_+I_z)+a_{1-}(I_zI_-+I_-I_z)+a_{2+}I_+^2+a_{2-}I_-^2\}|\Psi_m^0\rangle. \quad (1)$$

This form is the same as Eq. (1) of Han and Kessemeier [1] except that the matrix elements in the Ψ_m^0 representation are shown explicitly [2]. In this representation, the Zeeman Hamiltonian is diagonal, whereas the quadrupole Hamiltonian contains off-diagonal terms, as can be seen from (1).

Expression of H_Q in the Ψ_m^{ZQ} basis can be done as a perturbation series in ω_Q/ω_L, where ω_L is the Larmor frequency (strength of the Zeeman Hamiltonian). In contrast to (1), H_Q in this representation will contain all powers of ω_Q. This procedure was followed by Han and Kessemeier [1] to third order, but we must note that the state basis is the Ψ_m^{ZQ}, not the Zeeman states. In this representation, the Zeeman Hamiltonian H_Z is not diagonal, and the off-diagonal matrix elements of H_Z *must* be included as well as those of H_Q, in determining the evolution of the density matrix.

In the Ψ_m^{ZQ} basis, H_Z+H_Q is diagonal, so density matrix evolution will be as outlined above: Elements ρ_{mn} are multiplied by a complex phase factor $\exp\{i(E_m^{ZQ}-E_n^{ZQ})t/\hbar\}$, equivalent to spin precession in a static field. The nonsecular elements of H_Q are exactly compensated by nonsecular elements of H_Z, giving no net relaxation of density matrix elements (once the effect of the refocusing pulse is considered). For instance, to first order we have

$$|\Psi_m^{ZQ}\rangle=|\Psi_m^0\rangle+\sum_{p\neq m}\frac{\langle\Psi_p^0|H_Q|\Psi_m^0\rangle|\Psi_p^0\rangle}{E_m^0-E_p^0}, \quad (2)$$

and direct calculation shows that $\langle\Psi_n^{ZQ}|H_Z|\Psi_m^{ZQ}\rangle=-\langle\Psi_n^0|H_Q|\Psi_m^0\rangle$ to first order, for $n\neq m$. The source of apparent relaxation due to H_Q matrix elements can be attributed to the neglect of H_Z matrix elements.

Echo relaxation in quadrupole-split systems has received several treatments; Fedders [3] gives a general formalism. Using the 0.20-G dipolar width for ^{29}Si [4], the flip-flop portion of the second moment [5] will yield a spin-diffusion contribution to the ^{11}B T_2, approximately 40 ms. Also 2×10^{20} cm^{-3} B in silicon is a concentration comparable to that of the ^{29}Si nuclei, and if distributed randomly, it is easy to show that a direct ^{11}B-^{11}B contribution will also be of order 40 ms, using the quadrupole-truncated dipolar coupling [5]. B clustering, though, might explain the observed [1] 340-μs decay (if locally the quadrupole field seen by neighbor B sites is equivalent). Evidence of electron clustering has been observed for P in Si near the metal-insulator transition, [6] and typically for diluted alloy concentrations of 10% or more yield dipolar widths comparable to the fully concentrated situation [5].

Alternatively, low-frequency fluctuations can produce spin-echo decay, and are more likely to produce an exponential decay than a dipolar mechanism. An enhanced low-frequency spin-fluctuation spectrum has been deduced from the ^{29}Si T_1 of phosphorous-doped silicon at low temperatures [7], which makes this mechanism seem reasonable; the temperature dependence may provide a strong clue.

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