

Dephasing of Atomic Tunneling by Nuclear Quadrupoles

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Recent experiments revealed a most surprising magnetic-field dependence of coherent echoes in amorphous solids. We show that a novel dephasing mechanism involving nuclear quadrupole moments is the origin of the observed phenomena.

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Until recently, it was the general belief that the dielectric properties of insulating glasses—free of magnetic impurities—are largely independent of external magnetic fields. New investigations, however, revealed a strong variation at very low temperatures ($T < 100$ mK) for certain multicomponent glasses [1–7]. In particular, the low-frequency dielectric susceptibility and the amplitude of spontaneous polarization echoes generated in these amorphous materials show a striking nonmonotonic dependence on applied magnetic field.

Since the low-temperature properties of glasses are governed by atomic tunneling systems (for recent reviews, see [8,9]), it has been speculated whether and how a magnetic field can couple to quantum tunneling. Two models have been proposed that relate the magnetic-field dependence to the Ahanorov-Bohm phase of a charged particle moving along a closed loop [10,11]. Very recent polarization echo experiments, however, indicate that such a periodic variation of the tunnel splitting is not the origin of the observed magnetic-field effects [6,7]. In contrast, these experiments strongly suggest that nuclear magnetic moments play a crucial role in the observed anomalies.

In this Letter, we discuss how nuclear magnetic and quadrupolar moments influence atomic tunnel states. After a brief reminder of two-pulse echoes of two-level systems and the nuclear spin Hamiltonian, we give the echo-amplitude correction factor due to nuclear spins and evaluate this expression for the limiting cases of weak and strong magnetic fields. Finally, we compare our theory with recent data for several glasses.

Two-level systems (TLS) in glasses arise from double-well potentials with asymmetry Δ and tunnel matrix element Δ_0 ,

$$H = -\frac{1}{2}\Delta_0\sigma_x - \frac{1}{2}\Delta\sigma_z, \quad (1)$$

where $\sigma_z = \pm 1$ is the reduced two-state variable that indicates the states localized in the two wells [8,9]. The eigenstates ψ_0 and ψ_1 are separated by the energy splitting $E = \sqrt{\Delta_0^2 + \Delta^2}$ (see Fig. 1.) In a two-pulse echo experiment, the first pulse creates a coherent superposition of the ground state and the excited state, with a

relative phase factor $e^{-iEt/\hbar}$. Because of the dispersion of the two-level splitting E , the corresponding macroscopic polarization decays rapidly. After a waiting time t_w , the second pulse exchanges the amplitudes of these two states; the resulting phase factor $e^{-iE(t-t_w)/\hbar}$ leads to a revival of the coherent polarization, and the “echo” is observed at a time $t \approx t_w$ after the second pulse,

$$P_0(t, t_w) = \sum_i A_i \cos[\omega_i(t - t_w)], \quad (2)$$

where the sum runs over all TLS with tunnel frequency $\omega_i = E_i/\hbar$ and effective dipole moment A_i .

Such a tunnel system involves several atoms, each of which may carry a nuclear magnetic dipole and an electric quadrupole. For the sake of simplicity, we consider a single atom whose nucleus is in a state of total angular momentum \mathbf{I} , where $\mathbf{I}^2 = \hbar^2 I(I+1)$. This “nuclear spin” results in a magnetic moment $g\mu_N\mathbf{I}/\hbar$, with the Landé factor g and the nuclear magneton $\mu_N = 5 \times 10^{-27}$ J/T. In the case $I \geq 1$, the orbital motion of the protons is related to an electric quadrupole moment [12]; for a nuclear charge distribution $\rho(\mathbf{r})$ oriented along the axis \mathbf{e} , one finds

$$Q = \int d^3r [3(\mathbf{r} \cdot \mathbf{e})^2 - r^2] \rho(\mathbf{r}). \quad (3)$$

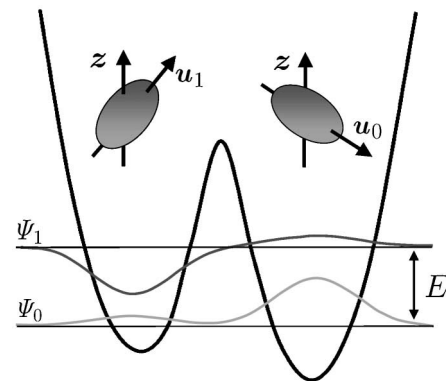


FIG. 1. Two-level system with energy splitting E , eigenfunctions ψ_0 and ψ_1 , and the corresponding quadrupole quantization axes \mathbf{u}_0 and \mathbf{u}_1 .

The magnetic dipole couples to the external field $\mathbf{B} = B\mathbf{e}_z$ and the quadrupole moment to the electric-field gradient (EFG) that is given by the curvature of the crystal field potential $\phi(\mathbf{r})$. We consider the simplest case of a single diagonal term $\phi'' = (\mathbf{u} \cdot \nabla)^2 \phi$ along the axis \mathbf{u} . Then the spin Hamiltonian reads as [12]

$$V = g\mu_N B \hat{I}_z + \frac{\phi'' Q 3\hat{I}_u^2 - I(I+1)}{4 I(2I-1)}, \quad (4)$$

with the projections of the nuclear spin operator on the axes defined by the EFG, $\hat{I}_u = (\mathbf{u} \cdot \mathbf{I})/\hbar$, and the magnetic field, $\hat{I}_z = I_z/\hbar$.

For zero magnetic field, \mathbf{u} is the appropriate quantization axis; with $\hat{I}_u^2 = m^2$ and $m = -I, \dots, I$, the Hamiltonian is diagonal. ($I = 1$ and $I = 3/2$ give rise to a doublet, $I = 2$ and $I = 5/2$ to a triplet, etc.) In the opposite case of zero EFG, the usual choice $\hat{I}_z = m$ gives the $(2I + 1)$ Zeeman levels $mg\mu_N B$. In general, the axes defined by the magnetic field, \mathbf{e}_z , and the EFG, \mathbf{u} , are not parallel; i.e., the operators \hat{I}_u and \hat{I}_z cannot be diagonalized simultaneously, thus resulting in a more complicated situation if both the magnetic field and the EFG are finite.

For asymmetric TLS, one of the eigenstates, say, the ground state ψ_0 , has a large probability amplitude in the right well, whereas the excited one, ψ_1 , has a larger amplitude in the left well (see Fig. 1.) In an amorphous or disordered solid, the crystal field, and thus the quadrupole quantization axis, are not the same in the two wells. In terms of the nuclear spin Hamiltonian, this means that both the absolute value of the EFG and the quantization axis depend on the two-state variable. These quantities are denoted ϕ_0'' and \mathbf{u}_0 in the ground state and ϕ_1'' and \mathbf{u}_1 in the excited level.

Now we discuss how nuclear spins affect the polarization echo that arises from a coherent superposition of the two tunnel states. In general, the quadrupolar part of

the nuclear spin Hamiltonian does not commute with H . Thus, V leads to a dispersion of the two-level splitting when switching from \mathbf{u}_0 to \mathbf{u}_1 during the two pulses and, thus, to a dephasing of the echo signal.

The density operator of a TLS involves four independent operators, e.g., the three Pauli matrices $\sigma_x, \sigma_y, \sigma_z$, and unity. Accordingly, the propagator is represented by a four-dimensional matrix [13]. Taking into account a nuclear spin I renders the dynamics significantly more complex, since we have to deal with $D = 2(2I + 1)$ quantum states corresponding to a density matrix with D^2 entries. It can be shown that a nuclear spin results in an overall factor of the echo amplitude [14],

$$P(t, t_w) = P_0(t, t_w) f(t, t_w), \quad (5)$$

where $f(t, t_w)$ is determined by the nuclear spin energies and eigenfunctions in the upper and lower tunnel states,

$$f(t, t_w) = \overline{\sigma_z e^{-i\mathcal{L}t} \mathcal{R}(\Omega\tau_2) e^{-i\mathcal{L}t_w/\hbar} \mathcal{R}(\Omega\tau_1)}. \quad (6)$$

The bar indicates the ensemble average; time evolution for zero driving field is written in terms of the Liouville operator $\mathcal{L}^* = (1/\hbar)[V, *]$, and the rotations \mathcal{R} account for the two electric-field pulses of duration τ_i and Rabi frequency Ω . Both \mathcal{L} and \mathcal{R} are superoperators that act on nuclear spin variables. The argument of $\mathcal{R}(\theta)$ is the ‘‘pulse area’’ θ .

The first external-field pulse creates a coherent superposition of the two tunnel states, whereas the second pulse exchanges their phases. (In the Bloch spin picture, this is related to rotations of the ‘‘polarization vector’’ $\langle \vec{\sigma} \rangle$.) The full density matrix is expressed through standard basis operators $|\mathbf{u}_i\alpha\rangle\langle\mathbf{u}_j\beta|$, with $i, j = 0, 1$ and $\alpha, \beta = -I, \dots, I$. In the composite space of TLS and nuclear spin variables, \mathcal{L} and \mathcal{R} are represented by tetrads L_{pqrs} and R_{pqrs} of dimension D^4 . Spelling out the matrices \mathcal{R} and σ_z and taking the trace, we obtain the correction factor

$$f(t, t_w) = \sum_{\alpha\beta\gamma\delta} \overline{f_{\alpha\beta\gamma\delta} \cos[(\varepsilon_{0\alpha} - \varepsilon_{1\beta})t/\hbar - (\varepsilon_{0\gamma} - \varepsilon_{1\delta})t_w/\hbar]}, \quad (7)$$

where nuclear spin energy levels (i.e., the eigenvalues of V) are denoted by $\varepsilon_{0\alpha}$ and $\varepsilon_{1\alpha}$ and $f_{\alpha\beta\gamma\delta}$ depends on the matrix elements of \mathcal{R} and σ_z . (Details will be given elsewhere [14].) Here we resort to a simple approximation that is justified in various situations, such as short pulses or almost parallel quadrupolar quantization axes, and that is expected to grasp the essential physics in any case. Since the polarization echo occurs on a time scale much shorter than the waiting time, we may put $t = t_w$. For a TLS initially in the ground state, we find the phase factor

$$f(t_w) = \frac{1}{2I+1} \sum_{\alpha,\beta,\delta} \overline{|\chi_{\alpha\beta}|^2 |\chi_{\alpha\delta}|^2 \cos(\omega_{\beta\delta} t_w)}, \quad (8)$$

that depends on the overlaps

$$\chi_{\alpha\beta} = \langle \mathbf{u}_0\alpha | \mathbf{u}_1\beta \rangle \quad (9)$$

and the quadrupole spectrum

$$\omega_{\beta\delta} = (\varepsilon_{1\delta} - \varepsilon_{1\beta})/\hbar. \quad (10)$$

For the case where the system is initially in the excited state, we find a similar expression with $\varepsilon_{0\gamma}$ instead of $\varepsilon_{1\gamma}$. Thus, $f(t_w)$ describes the reduction of the whole echo signal.

In the remainder of this Letter, we discuss the reduction factor (8). First we consider the situation where the quadrupole coupling is ineffective, such as a zero EFG, parallel quantization axes $\mathbf{u}_0 = \mathbf{u}_1$, or a very strong magnetic field. Then the nuclear spin states corresponding to

the tunnel levels are identical, $|\mathbf{u}_0\alpha\rangle = |\mathbf{u}_1\alpha\rangle$, for $\alpha = -I, \dots, I$ and $\chi_{\alpha\beta} = \delta_{\alpha\beta}$, resulting in $f(t_w) \equiv 1$.

In general, however, the EFG is finite and the quadrupolar Hamiltonian is not the same for the two levels, resulting in a nondiagonal overlap matrix, $\chi_{\alpha\beta}$. The quadrupolar energy scale reads as

$$\hbar\omega_Q = \frac{3}{4I(2I-1)}\phi''Q. \quad (11)$$

Typical values for the quadrupolar energy $\phi''Q$ correspond to frequencies of the order of tens of MHz and thus satisfy, for waiting times $t_w \sim \mu$ sec, the inequality $\omega_Q t_w \gg 2\pi$ that simplifies significantly the analysis. As a consequence, all terms involving different quadrupole levels $\delta \neq \pm\beta$ in (8) vanish. Yet note that the quadrupolar spectrum exhibits a degeneracy with respect to $\beta \rightarrow -\beta$ which, in turn, is lifted by a magnetic field.

In the limit of zero waiting time, the cosines in (8) are equal to unity, and we have $f(t_w \rightarrow 0) = 1$. In the opposite case of very long times and all degeneracies lifted, the terms with finite frequency $\omega_{\delta\beta}$ vanish, resulting in

$$f(t_w \rightarrow \infty) = \frac{1}{2I+1} \sum_{\alpha,\beta} |\chi_{\alpha\beta}|^4 = 1 - a. \quad (12)$$

We are interested in the intermediate regime of experimentally relevant waiting times that are of the order of μ sec. Thus, we have to look for frequencies in the MHz range that satisfy the condition $\omega_{\delta\beta} t_w \sim \pi$.

Both the overlaps $\chi_{\alpha\beta}$ and the frequencies $\omega_{\gamma\beta}$ depend in an intricate manner on the relevant orientation of the three vectors \mathbf{e}_z , \mathbf{u}_0 , \mathbf{u}_1 and on the ratio of the Zeeman splitting and the quadrupolar energy. Here we discuss a few limiting cases where (8) simplifies significantly. The argument is developed for half-integer spin $I = \frac{3}{2}, \frac{5}{2}, \dots$ but is easily generalized to integer I .

First we consider the case of a weak magnetic field, where

$$\hbar\omega_Z = g\mu_N B \quad (13)$$

is small as compared to $\hbar\omega_Q$. Then the nuclear Zeeman splitting $\hbar\omega_Z$ lifts the degeneracy of the doublets $\pm\beta$ of the quadrupolar energy ($\beta = \frac{1}{2}, \dots, I$). Discarding rapidly oscillating terms $\sim \cos(\omega_Q t_w)$ and separating the weight factor

$$b_\beta = 2 \sum_{\alpha} |\chi_{\alpha\beta}|^2 |\chi_{\alpha,-\beta}|^2$$

and the time-dependent term, we obtain

$$f(t_w) = 1 - a + \sum_{\beta} b_{\beta} \overline{\cos(\omega_{\beta,-\beta} t_w)}. \quad (14)$$

For small B we may neglect the magnetic-field dependence of the weight factors and treat the Zeeman term as a perturbation. Starting from the eigenbasis of the quadrupolar energy, we thus diagonalize the Zeeman term

of V in each degenerate subspace $\pm\beta$. The splitting of each doublet $\pm\beta$ depends on the relative orientation of the quantization axes \mathbf{e}_z and \mathbf{u}_1 through the cosine $x = \mathbf{e}_z \cdot \mathbf{u}_1$. For $\beta = \frac{3}{2}, \dots, I$, the splitting is given by the projection of the magnetic field on the quadrupolar axis,

$$\omega_{\beta,-\beta} = x2\beta\omega_Z \quad (\beta > 1/2), \quad (15)$$

whereas for $\beta = \frac{1}{2}$, it reads as

$$\omega_{1/2,-(1/2)} = \sqrt{x^2 + (I+1/2)^2(1-x^2)}\omega_Z. \quad (16)$$

The average in (14) is given by

$$\overline{(\dots)} = \int_0^1 dx p(x)(\dots). \quad (17)$$

Though possible in principle, calculation of the normalized distribution $p(x)$ is beyond the scope of the present Letter. Equation (14) shows oscillatory behavior with period $\sim \omega_Z t_w$, independent of the precise form of $p(x)$. For $I = \frac{3}{2}$ there are two components; using $p(x) = 1$, their minima occur at $\omega_Z t_w \approx 0.6\pi$ ($\beta = \frac{1}{2}$) and $\omega_Z t_w \approx 0.5\pi$ ($\beta = \frac{3}{2}$); regarding Al ($I = \frac{5}{2}$) there are three features with minima at $\omega_Z t_w \approx 0.4\pi, 0.5\pi, 0.3\pi$ (see Table I.) For the fit of the experimental data in Fig. 2, the best results are obtained with $p(x) = 3x^2$ and $b_{1/2} = 2b_{3/2}$.

Now we turn to strong magnetic fields, $\omega_Z \gg \omega_Q$, where the quadrupole energy may be treated as a perturbation with respect to the Zeeman splitting. When calculating the overlap matrix $\chi_{\alpha\beta}$ to lowest order in ω_Q/ω_Z and observing the normalization condition $\sum_{\beta} |\chi_{\alpha\beta}|^2 = 1$, we obtain

$$1 - f(t_w) = 2 \sum_{\alpha,\beta \neq \alpha} |\chi_{\alpha\beta}|^2 \sim \left(\frac{\hbar\omega_Q}{g\mu_N B} \right)^2. \quad (18)$$

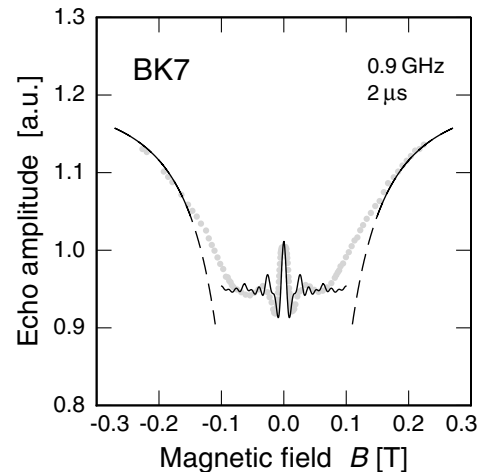


FIG. 2. Magnetic-field dependence of the echo amplitude of BK7 [15]. The solid lines are calculated as explained in the text.

TABLE I. Nuclear spin parameters g and I . Experimental values for the first minimum of the echo amplitude. Calculated values for $\beta = 1/2, \dots, I$, as explained in the text. The natural abundance of $^{135/137}\text{Ba}$ is 17%.

		I	g	(Meas.) $B_{\min}t_w$	(Calc.) (10^{-9} Ts)
Borosilicate	^{11}B	3/2	1.8	22	21/18
KBr:CN	$^{79,81}\text{Br}$	3/2	1.5	30	25/21
Al-Ba-silicate	^{27}Al	5/2	1.44	28	18/22/13
	$^{135/137}\text{Ba}$	3/2	0.6		63/52

Thus, we find a variation $f(t_w) = 1 - \text{const} \times B^{-2}$ at high magnetic fields, as shown in Fig. 2.

These theoretical findings (14)–(18) agree rather well with available data. We briefly discuss the most salient features.

(i) Both the oscillatory behavior of the echo amplitude with small B and the saturation at higher fields have been observed for several multicomponent glasses and mixed crystals [6,7]. In Fig. 2 we plot the echo amplitude measured for the borosilicate glass BK7 as a function of the magnetic field. At small B the data show a few oscillations; at higher fields the amplitude increases strongly and would seem to saturate. The solid line for $B < 100$ mT is calculated from Eq. (14) that, with $t_w = 2\mu$ sec, $g = 1.8$, and $I = \frac{3}{2}$, describes the first minimum unambiguously. The increase at $B > 100$ mT has been fitted with (18).

(ii) The particular waiting time dependence of the echo amplitude through the product Bt_w has been verified experimentally in great detail, especially for KBr:CN [7]. In Table I we give the nuclear spin parameters I and g and the measured and calculated positions of the first minimum in terms of the quantity $B_{\min}t_w$.

(iii) All systems showing the magnetic-field dependence contain nuclei with $I \geq 1$ and finite quadrupole moments (B in BK7; Br and N in KBr:CN; Al in Ba-Al-silicate). On the other hand, the only glass that shows no magnetic-field dependence (amorphous silicon oxide) [15] does not contain nuclear quadrupoles, since $I = \frac{1}{2}$ for ^{29}Si and $I = 0$ for ^{16}O and ^{28}Si .

These findings provide very strong evidence that the observed magnetic-field dependence arises from the dynamic phase of the nuclear Zeeman splitting of quadrupolar levels. (Preliminary experiments on other systems would seem to confirm this statement [15].) The simplifications of the present theory may be at the origin of the discrepancies in Fig. 2. For example, real tunnel systems certainly involve more than one nuclear spin. This is obvious for glasses. In mixed crystals, the tunneling atom drags its dressing cloud; that is why bromine appears in Table I. The present theory shows no temperature

dependence, since the time evolution in (6) is purely coherent and does not account for relaxation.

It seems likely at this point that the quadrupole splitting of tunneling levels not only influences the amplitude of polarization echoes, but has also consequences for other properties of glasses at very low temperatures. In particular, we expect that the magnetic-field dependence of the dielectric susceptibility observed in several glasses is also caused by nuclear spins.

In summary, we have proposed an explanation for the recently observed magnetic-field dependence of polarization echoes in terms of a novel dephasing mechanism involving nuclear spins and quadrupole moments. The EFG ϕ'' and the corresponding axes \mathbf{u} are not the same in the two minima of the atomic double-well potential; the quadrupolar energies give rise to phase dispersion that reduces the echo signal. The oscillations at small fields result from the interference of the dynamical quantum phases of almost degenerate quadrupole levels. The strong increase of the echo amplitude at larger B is due to the alignment of the nuclear magnetic moments with respect to the magnetic field. For strong fields, $\mu_N B \gg \hbar\omega_Q$, we expect saturation at the value $f = 1$.

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