Oscillations of Echo Amplitude in Glasses in a Magnetic Field Induced by Nuclear Dipole-Dipole Interaction.

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(Dated: November 22, 2009)

The effect of a magnetic field on the dipole echo amplitude in glasses (at temperatures of about 10 mK) induced by the dipole-dipole interaction of nuclear spins has been theoretically studied. It has been shown that a change in the positions of nuclear spins as a result of tunneling and their interaction with the external magnetic field \( E_B \) lead to a nonmonotonic magnetic field dependence of the dipole echo amplitude. The approximation that the nuclear dipole-dipole interaction energy \( E_d \) is much smaller than the Zeeman energy \( E_H \) has been found to be valid in the experimentally important cases. It has been shown that the dipole echo amplitude in this approximation may be described by a simple universal analytic function independent of the microscopic structure of the two-level systems. An excellent agreement of the theory with the experimental data has been obtained without fitting parameters (except for the unknown echo amplitude).

PACS numbers: 61.43.Fs, 76.60.-k, 81.05.Kf

I. INTRODUCTION

Glasses at temperatures below 1 K are known to exhibit a number of universal properties almost independent of their composition and fundamentally different from the properties of similar crystals. These properties are traditionally described within the model of two-level systems (TLS's) \([\text{1}]\). One of these properties is a two-pulse electric dipole echo in glasses, which is the delayed response to two high-frequency electromagnetic pulses.

When a glass is subjected to two rf pulses with a frequency of about 1 GHz separated by a time interval \( \tau \) much longer than the pulse length, one can observe a response in the glass polarization at time \( \tau \) after the second pulse. Especially interesting is the pronounced nonmonotonic magnetic field dependence of the two-pulse echo amplitude observed at temperatures of 10 mK in the absence of paramagnetic centers in the glass \([\text{2}]\). The nature of this interesting phenomenon remained unclear until works \([\text{3, 4, 5, 6}]\), where this dependence was associated with the presence of atoms with a nuclear quadrupole moment in the glass.

Owing to the interaction of the nuclear magnetic moment with the external magnetic field (Zeeman interaction) and the nuclear quadrupole moment with the gradient of the internal electric field, the levels of the TLS split into two nearly identical series of levels. The characteristic energies of such a fine structure are \( 10^{-21} \) erg (corresponding to a frequency of about 100 kHz), which are much lower than the typical energy of 50 mK of the TLS’s specified by the 1 GHz frequency of the excitation pulses. Since the internal field gradient is different at different positions of the TLS’s, the fine level structure depends on the tunneling state of the TLS, which ultimately leads to the nonmonotonic magnetic field dependence of the dipole echo amplitude \([\text{3, 4, 5}]\).

As a proof of this hypothesis, the results on measuring the two-pulse echo amplitude in glycerol (C\(_3\)H\(_8\)O\(_3\)) were presented \([\text{4}]\). In this experiment the echo amplitude dependence on magnetic field increased by more than an order of magnitude under the replacement of hydrogen with zero nuclear quadrupole moment by deuterium (whose nuclear spin is 1 so deuterium has a small quadrupole moment).

The oscillations of the echo amplitude in a magnetic field were theoretically studied in \([\text{1, 2, 4, 5, 6}]\). In particular, the qualitative explanation of the observed effect was given in \([\text{3, 4, 5}]\). In \([\text{3, 4}]\), numerical calculations of the dipole echo amplitude in glycerol in the magnetic field were performed and a good agreement with the experimental data was obtained.

In our previous work \([\text{9}]\), we qualitatively and, in some cases, quantitatively compared our analytic expressions for the echo amplitude in glasses containing nuclear electric quadrupole moments with the experimental data. However, the existence of small oscillations of the dipole echo amplitude in glasses containing only spherical nuclei (without quadrupole moments), like in nondeuterated glycerol C\(_3\)H\(_8\)O\(_3\), remained unexplained until papers \([\text{7, 8}]\). The presence of a small (0.037%) natural impurity of the \(^{17}\)O isotope, which also has a nuclear quadrupole moment, did not explain these oscillations.

Fleishmann \([\text{7}]\) suggested that the magnetic field dependence of the echo amplitude in the case of nondeuterated C\(_3\)H\(_8\)O\(_3\) may be caused by the dipole-dipole interaction of the nuclear magnetic moments of hydrogen atoms (the spin and, respectively, the magnetic moment of the primary isotopes of carbon \(^{12}\)C and oxygen \(^{16}\)O are zero). This interaction (along with the Zeeman interaction) induces a fine structure of the levels of the TLS, which depends on the tunneling states of the systems.

Bazrafshan et al. \([\text{8}]\) numerically calculated the echo...
amplitude in deuterated glycerol C₄D₃H₅O₃ (taking into account all of the spins of hydrogen and the quadrupole moments of deuterium). It was assumed that the tunneling of the two-level system is the rotation of the glycerol molecule as a whole. Although the theory was in a good agreement with the experiment in high fields and in semi-quantitative agreement in low magnetic fields (when the dipole-dipole interaction is responsible for the effect), the assumption of the rotational character of tunneling was not justified.

This work is aimed at obtaining the analytical results for the magnetic field dependence of the dipole echo amplitude in the absence of nonspherical nuclei in the glass, so that only the dipole-dipole interaction of the nuclear spins is taken into account, and at comparing the results with the experimental data on non-deuterated glycerol.

II. GENERAL THEORY OF THE MAGNETIC FIELD DEPENDENCE OF THE ECHO AMPLITUDE

Parshin [6] derived a general formula specifying the dipole echo amplitude in an arbitrary system, which consists of two identical sets of levels separated by an energy gap much larger than the splitting within the sets

\[ P_{\text{echo}} \propto -\frac{i}{N} V_1 V_2^2 \cdot \sum_{n,k} \left| e^{i(E_n - E_k)\tau / \hbar} \sum_m \alpha_{nm}^{(12)} \gamma_{km}^{(12)} e^{iE_m \tau / \hbar} \right|^2. \]  

(1)

Here, \( P_{\text{echo}} \) is the dipole echo amplitude; \( V_1 \) and \( V_2 \) are the amplitudes of the first and second exciting electric pulses, respectively; \( E_n \) are the fine-structure energy levels of the TLS; \( N \) is the total number of this levels, and \( \alpha_{nm}^{(12)} \) is the matrix element for the transition between the \( n \)-th lower and \( m \)-th higher levels of the split TLS during the action of the excitation pulses.

To use this formula, we have to find the fine-structure energy levels and the matrix elements of the transition in an arbitrary magnetic field. For that, let us write the Hamiltonian of the system including, first, the tunneling of the TLS atoms and, second, the energies of the nuclear spins, which form the fine level structure:

\[ \hat{H}_{\text{tot}} = \hat{H}_{\text{tls}} \otimes \hat{J}_J + \hat{\mathbf{I}}_{1s} \otimes \hat{W}_J + \sigma_{z,\text{tls}} \otimes \hat{V}_J + (\mathbf{d}_{\text{tls}} \cdot \mathbf{F}) \otimes \hat{1}_J. \]

(2)

Here \( \hat{H}_{\text{tls}} \) is the Hamiltonian of the TLS in the coordinate representation (excluding the fine structure); \( \hat{\mathbf{I}}_{1s} \) and \( \hat{1}_J \) are the identity matrices in the spaces of the TLS (2 × 2) and the nuclear spin projections, respectively; \( \sigma_{z,\text{tls}} \) is the Pauli matrix for the two-level system; \( \mathbf{d}_{\text{tls}} = \sigma_{z,\text{tls}} \) is the operator of the electric dipole moment \( \mathbf{d} \) of the TLS; and \( \mathbf{F} \) is the external (excitation) electric field.

The spin operators \( \hat{W}_J \) and \( \hat{V}_J \) are, respectively, the symmetric and antisymmetric (with respect to the TLS displacement) parts of the spin Hamiltonian

\[ \hat{H}_{J(1,2)} = \sum_i \mu_i \mathbf{H} + \frac{1}{2} \sum_{ij} \left[ \frac{\mu_i \mu_j}{r_{ij}^3} - 3 \left( \frac{\mu_i r_{ij}}{r_{ij}^5} \right) \left( \frac{\mu_j r_{ij}}{r_{ij}^5} \right) \right]. \]

(3)

Here \( \mu_i = \mu_0 \mathbf{J}_i / J_i \) is the operator of the magnetic moment of the \( i \)-th nuclei, \( \mathbf{J}_i \) is the operator of its spin, and \( \mathbf{H} \) is the external magnetic field. The radius vector \( r_{ij} \equiv r_{ij}^{(1,2)} \) from the \( i \)-th to the \( j \)-th nuclei may depend on the TLS position (1) or (2). The summation is performed over all tunneling nuclei. Consequently,

\[ \hat{W}_J = \frac{\hat{H}_{J(1)} + \hat{H}_{J(2)}}{2}, \quad \hat{V}_J = \frac{\hat{H}_{J(1)} - \hat{H}_{J(2)}}{2}. \]

(4)

Note that the first term of spin Hamiltonian (3), which is associated with the external magnetic field (the Zeeman part), does not include vectors \( \mathbf{r}_{ij} \) that change under tunneling of the TLS and, therefore, does not contribute to the antisymmetric \( \hat{V}_J \) part of the Hamiltonian. The dipole-dipole interaction (the second term of Hamiltonian (3)) enters both operators \( \hat{W}_J \) and \( \hat{V}_J \).

To find the quantities associated with the fine level structure, let us rewrite Hamiltonian (2) in the basis consisting of the stationary wavefunctions of the bottom and top levels of the TLS and the eigenfunctions of the operator \( \hat{W}_J \) for the spin variables:

\[ \hat{H}_{\text{tot}} = \frac{1}{2} \begin{pmatrix} E & 0 \\ 0 & -E \end{pmatrix} \otimes \hat{1}_J + \hat{\mathbf{I}}_\sigma \otimes \hat{W}_J + \mathbf{F} \cdot \mathbf{d} \frac{1}{E} \begin{pmatrix} \Delta & \Delta_0 \\ \Delta_0 & -\Delta \end{pmatrix} \otimes \hat{1}_J + \frac{1}{E} \begin{pmatrix} \Delta & \Delta_0 \\ \Delta_0 & -\Delta \end{pmatrix} \otimes \hat{V}_J. \]

(5)

Here, \( \Delta \) is the difference between the minima of the double-well potential, \( \Delta_0 \) is the tunneling amplitude of the initial (unsplit) TLS, and \( E = \sqrt{\Delta^2 + \Delta_0^2} \) is the total energy of the TLS (without the inclusion of the fine-structure effects). The tilded operators \( \hat{\mathbf{W}}_J \) and \( \hat{\mathbf{V}}_J \) correspond to the choice of the eigenfunctions of \( \hat{\mathbf{W}}_J \) as the basis. In this basis, \( \hat{\mathbf{W}}_J \) is a diagonal matrix.

We assume that the characteristic tunneling lengths of the nuclei are much shorter than the characteristic interatomic distances and, consequently, \( \hat{\mathbf{V}}_J \) is much smaller than \( \hat{\mathbf{W}}_J \) and may be taken into account perturbatively.

Retaining only the terms proportional to \( \hat{\mathbf{V}}_J \) in the transition matrix elements, we obtain the dipole echo ampli-
where $J$ observed in the magnetic fields this interaction should be retained in $\hat{E}$ contain terms of the order of magnitude smaller than the Zeeman energy.

The simplest case of two interacting spins 1/2 of no more than two spin projections are nonzero. This allows us to reduce the problem of an arbitrary number of fine-structure levels to the problem of two interacting spins to the problem of two interacting spins to the problem of two hydrogen nuclei at a distance of 1.9 Å (the minimum distance between hydrogen atoms in glycerol) may be estimated as $E_d \approx 1.5 \times 10^{-22}$ erg, which is almost an order of magnitude smaller than the Zeeman energy.

III. WEAK DIPOLE-DIPOLE INTERACTION APPROXIMATION

In the $E_d \ll E_H$ approximation, we neglect the dipole-dipole interaction in the expression for $\hat{W}_J$. However, this interaction should be retained in $\hat{W}_J$, which does not contain terms of the order of $E_H$.

In this approximation, the eigenfunctions of $\hat{W}_J$ are the states with definite projections of all nuclear spins on the direction of the magnetic field. In this case, only the matrix elements $(\hat{V}_J)_{nm}$ of the transition with a change of no more then two spin projections are nonzero. This allows us to reduce the problem of an arbitrary number of dipole-dipole interacting nuclear spins to the problem of one pair of spins. We consider only the pairs of identical spin 1/2 nuclei. The operator $\hat{W}_J$ may be then written in the form

$$\hat{W}_J = \mu H (\hat{J}_1 + \hat{J}_2),$$

where $\mu$ is the nuclear magnetic moment and $\hat{J}_1$ and $\hat{J}_2$ are the spin operators of the interacting nuclei. The matrix form of $\hat{W}_J$ is

$$\hat{W}_J = \left( \begin{array}{cccc} 2\mu H & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -2\mu H \end{array} \right).$$

It is easy to see that, in this case, there are four energy differences $\varepsilon_{nm}$ equal to $2\mu H$ and one difference $\varepsilon_{14} = 4\mu H$ ($\varepsilon_{23}$ is zero and does not contribute to the echo amplitude).

To express the echo amplitude explicitly with the use of Eq. (6), we need to calculate also the average squares of the matrix elements $|(\hat{V}_J)_{nm}|^2$. Taking into account the smallness of the tunneling length, the $\hat{V}_J$ operator in the case of two nuclei can be represented as

$$\hat{V}_J = \delta r_{12} \cdot \frac{\partial}{\partial r_{12}} \left[ \mu_1 \mu_2 r_{12} \left( 3 (\mu_1 r_{12}) (\mu_2 r_{12}) - r_{12}^2 \right) \right].$$

Expressing the gradient explicitly and taking out $\delta r_{12}$, $r_{12}$ and $\mu_{1,2}$ as the common factors, we may rewrite Eq. (10) in the form

$$\hat{V}_J = \mu^2 \delta r_{12} r_{12}^{-1} \sigma_{1,\alpha} \sigma_{2,\beta} N_{\alpha,\beta} (n_r, \xi) \delta r \delta r.$$
any fitting parameters (except for the constant \( C \), which specifies the vertical scale) until the region of small magnetic fields (\( \leq 1 \text{ mT} \)), where the conditions \( E_H \ll E_d \) seemingly breaks.

### A. Applicability Conditions

The nonmonotonic magnetic field dependence of the dipole echo amplitude is determined by the term \( \sin^4(\varepsilon_{nm}\tau/2\hbar) \) in Eq. (6). This corresponds to the characteristic energies \( \varepsilon_{nm} \approx 2\hbar/\tau \). In the case of \( E_d \ll 2\hbar/\tau \) (or, equivalently, \( \tau \ll 2\hbar/E_d \)), we may expect that the condition \( E_d \ll E_H \) holds for the dominant part of the dependence. Otherwise, the exact inclusion of the dipole-dipole interaction is required; in this case, in particular, the problem cannot be reduced to the problem of two tunneling nuclei. This agrees well with the fact that the theory better describes the experimental data for \( \tau = 3.5 \mu s \) than for \( \tau = 8 \mu s \) (see figure) in the low-field region.

Note that the horizontal scale of the magnetic field dependence of the echo amplitude in the case under consideration is determined by the time \( \tau \). Thus, the curve \( P_{\text{echo}}(H) \) should scale in the horizontal axis as \( 1/\tau \) with a change in the time interval between the pulses. In the opposite case of \( \tau \gg 2\hbar/E_d \), the horizontal scale of the dependence is determined by the relation \( E_d \approx E_H \) and is independent of the time interval between the pulses. This may be used as an experimental criterion of the smallness of the dipole-dipole interaction.

To conclude, in the experimentally observed case of \( \tau \ll 2\hbar/E_d \), the magnetic field dependence of the dipole echo amplitude induced by the dipole-dipole interaction of the nuclei of the same kind has a universal character independent of the microscopic structure of the TLS. It is well described by a simple analytic expression. A good agreement of the theory and experiment on the dipole echo amplitude in nondeuterated glycerol was obtained without any fitting parameter (except for the echo amplitude scale). At larger values of the time interval between the excitation pulses, \( \tau \gtrsim 2\hbar/E_d \), the universal form of the dependence breaks, which may allow one to obtain information on the microscopic structure of the two-level systems with the use of numerical analysis [11].

We are grateful to A. Fleischmann and M. Bazrafshan for fruitful discussions.

A.V.S. thanks the St. Petersburg administration for support in 2008, candidate project no. 2.4/4-05/103.

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