Novel Isotope Effects Observed in Polarization Echo Experiments in Glasses

P. Nagel, A. Fleischmann, and S. Hunklinger
Kirchhoff-Institut für Physik, Universität Heidelberg, Im Neuenheimer Feld 227, D-69120 Heidelberg, Germany

C. Enss
Department of Physics, Brown University, Box 1843, Providence, Rhode Island 02912, USA
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In recent years unexpected magnetic field effects have been observed in dielectric measurements on insulating glasses at very low temperatures. Polarization echo experiments have indicated that atomic tunneling systems are responsible for these effects and that the nuclear properties of the tunneling particles are of importance. Subsequently, it was suggested that the magnetic field effects are caused by tunneling systems carrying a nuclear quadrupole moment. Now we have studied the isotope effect in echo experiments on fully deuterated and ordinary glycerol clearly showing the crucial role of the nuclear quadrupole moments for the magnetic field effects. In addition, we have observed a new effect in the decay of spontaneous echoes in zero magnetic field for the deuterated samples which can be explained in terms of a quantum beating involving the quadrupole levels.

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The low-temperature properties of glasses are governed by a broad distribution of low-energy excitations which are present in these materials in addition to the Debye-like phonon spectrum. These low-lying states originate from atoms or groups of atoms that can rearrange within the network structure of glasses by tunneling between adjacent potential minima [1,2]. Early evidence for the existence of the low-energy excitations in glasses was found more than 30 years ago in specific heat and thermal conductivity experiments [3]. A phenomenological description of the low-temperature physics of glasses is given by the so-called tunneling model [4,5], which assumes that particles are tunneling in double-well potentials and that the parameters describing these potentials are widely distributed. While many experimental results can be explained satisfactorily by this model some findings at very low temperatures seem incomprehensible with this simple picture (for a recent overview, see [6]).

One particular example of this kind is the unexpected magnetic field dependence discovered in the dielectric low-temperature properties of several multicomponent glasses in the past few years [7–11]. Before this discovery it was the general belief that the dielectric properties of insulating glasses free of magnetic moments would be hardly sensitive to magnetic fields. The first observation of a strikingly strong sensitivity of the dielectric constant to magnetic fields was made in experiments on the multicomponent glass a-BaO-Al_2O_3-SiO_2 [7]. At a temperature of 1.85 mK a magnetic field change of only 10 μT caused clear changes in the dielectric constant of this material. In subsequent experiments it was found that the dielectric constant and also the dielectric loss in this material and other multicomponent glasses varies nonmonotonically with the magnetic field. Two models have been proposed to explain these findings by a coupling of the magnetic field to looplike tunneling paths of mutually interacting charged tunneling particles [12,13].

Recent polarization echo experiments have shown that tunneling systems indeed couple to magnetic fields and have revealed more details about this coupling [14–16]. In these experiments the glass samples were placed in the uniform electric field region of a reentrant microwave cavity and two short rf pulses separated by a delay time t_{12} were applied. After a time $2t_{12}$ counting from the first pulse, a macroscopic polarization is recorded, the so-called spontaneous echo. The amplitude of this echo reflects the number and the coupling of tunneling systems maintaining phase coherence throughout the time period $2t_{12}$ [17]. In many ways such polarization echo experiments are analogous to the well-known two-pulse spin echo in NMR experiments. Surprisingly, the amplitude of the spontaneous echoes generated in several multicomponent glasses varied nonmonotonically with the external magnetic field, resembling in part what has been observed in the low-frequency dielectric measurements. In the case of the echo experiments, however, only tunneling systems being in resonance with the rf field contribute to the signal showing that there is some kind of direct coupling of the magnetic field to tunneling systems.

Moreover, echo experiments at different delay times t_{12} showed that certain features (maxima and minima of the echo amplitude as a function of the magnetic field) scale as the product $t_{12}B$, where B is the applied magnetic field [15,16]. The product $t_{12}B$ at which these features occur can be interpreted as a magnetic moment $h/(t_{12}B)$ and the corresponding values are of the order of a nuclear magnetic moment. This suggested that the nuclear spin of the tunneling particle plays role in the magnetic field dependence. At first glance an influence of the nuclear spins on a microsecond time scale seemed inconceivable because of the extremely long nuclear spin-lattice relaxation times in

insulating materials at low temperatures [18]. However, it was soon realized that the coupling of the tunneling motion to the nuclear degrees of freedom could be brought about by the nuclear quadrupole moment experiencing the electric field gradients in the two localized states of the double-well potential. This coupling gives rise to a quadrupole splitting of the energy levels of the tunneling systems. The applied magnetic field then leads to an additional Zeeman splitting of the nuclear levels. Based on this picture a detailed model has been worked out to explain the magnetic field effects in the polarization echo experiments [19].

In the work presented here we have investigated fully deuterated glycerol and ordinary glycerol [20] in polarization echo experiments to verify in a direct way the importance of the nuclear quadrupole moment of the tunneling particles to the magnetic field dependence of the echo amplitude. Glycerol is a good glass former, consisting of $C_3H_8O_3$ molecules. For a cooling rate of about 1 K/min the glass transition temperature is $T_g = 185$ K. The beauty of this system with respect to our investigation lies in the fact that practically none of these atoms is carrying a nuclear quadrupole moment and that the hydrogen can be substituted by deuterium which has nuclear spin $I = 1$ and a nuclear quadrupole moment. One other advantage of glycerol is that it has been investigated thoroughly by NMR spectroscopy so that quantitative results for the quadrupole splitting in these systems exist (see, for example, [21]).

In zero magnetic field the energy levels of the three nuclear spin states of a deuterium in glycerol are split into two due to the quadrupole moment of the deuterium and the electric field gradients associated with the sigma binding to either a carbon or an oxygen atom. Because of the axial symmetry of this binding the levels of the nuclear spin states $m_I = \pm 1$ are degenerate. This also holds in the glassy state in which a hydrogen bonded network is formed. With magnetic field B the nuclear levels $m_I = \pm 1$ exhibit an additional Zeeman splitting $g_I \mu_N B$. Furthermore, the quantization axis will in general tip away from the direction of the electric field gradient, because in the amorphous material the direction of the magnetic field and the electric field gradient do not necessarily coincide. At large fields $g_I \mu_N B \gg \hbar\omega_q$ the nuclear levels become approximately equidistant and the quantization axis is entirely determined by the direction of the magnetic field. Here $\hbar\omega_q$ denotes the quadrupole splitting.

The situation becomes considerably more complicated when a deuterium atom is part of a tunneling system. The energy splitting of a tunneling system is given by $E = \sqrt{\Delta^2 + \Delta_0^2}$, where Δ stands for the asymmetry energy due to the difference in the depth of the two wells and Δ_0 for the tunnel splitting originating from the overlap of the wave functions. If a deuterium now is a part of such a tunneling system the nuclear levels of the deuterium result in a fine splitting of these tunneling levels. In general the electric field gradient in the two wells of a tunneling potential does not point in a single direction as can easily be seen when assuming a rotational tunneling motion. The appropriate basis for describing the nuclear spin states in a tunneling system is thus a mixture of the pure spin states without the tunneling motion.

In zero magnetic field the intermediate state of such a system is a superposition of more than two states [19]. The echo amplitude caused by such a six-level system is reduced in comparison to that of a two-level system. As stated above, in large magnetic fields ($g_I \mu_N B \gg \hbar\omega_q$) the quantization axis of the nuclear spins is determined by the direction of the magnetic field. Therefore, no mixing of the different nuclear spin states occurs, and the echo amplitude is identical with that of a simple two-level system. Consequently, the echo amplitude is expected to increase with magnetic field and should reach a saturated level at high fields.

Figure 1 shows the amplitude of spontaneous echoes in fully deuterated and ordinary glycerol as a function of the magnetic field. While in the case of ordinary glycerol there is hardly any change of the echo amplitude visible a change of more than a factor of 2 is observed for fully deuterated glycerol. From the value at $B = 0$ the amplitude of the echo increases with the applied magnetic field and becomes constant at fields above about 150 mT. This dramatic isotope effect clearly proves the crucial role of the nuclear quadrupole moment in the magnetic field effects in echo experiments. As in previous experiments on multicomponent glasses, the form of the curve at low fields depends on the delay time t_{12} [16]. This variation is related to another effect which we will discuss at the end of the paper.

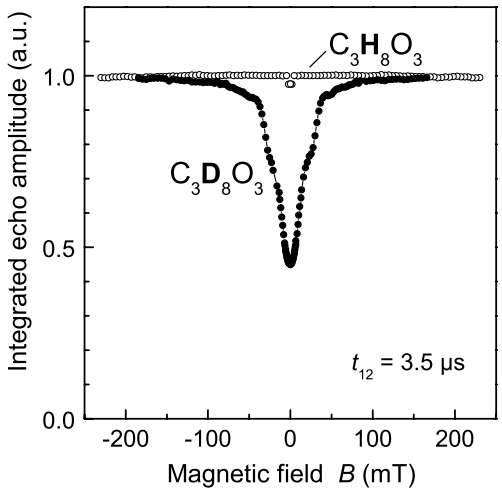

FIG. 1. Integrated amplitude of spontaneous echoes generated in fully deuterated glycerol and ordinary glycerol as a function of magnetic field. The data have been taken at 13.4 mK.

A closer inspection of Fig. 1 reveals another interesting phenomenon. The echo amplitude of ordinary glycerol is constant as a function of the magnetic field in the whole field range except for a tiny dip around $B = 0$. Figure 2 shows a blowup of this region. There is a clear systematic magnetic field variation, which looks qualitatively different from that of the fully deuterated sample. At zero magnetic field there appears a maximum of the echo amplitude much like in the case of multicomponent glasses and the saturation of the amplitude sets in already at very small magnetic fields. One possible explanation for the magnetic field dependence found in ordinary glycerol is that it is caused by both the natural abundance of deuterium (about 125 ppm) and of ^{17}O (about 500 ppm) present in ordinary glycerol. The isotope ^{17}O has nuclear spin $I = 5/2$ and therefore carries a quadrupole moment. The total variation of the echo amplitude is about 3%. Given the abundances as stated above roughly 0.1% of all glycerol molecules should contain a deuterium atom and 0.15% an ^{17}O atom. These numbers suggest that on average more than ten glycerol molecules are involved in an individual tunneling process. If this interpretation is correct it would be a very remarkable result, indicating that at very low temperatures tunneling systems in glasses are caused by the collective motion of many molecules. At this point, however, we cannot rule out completely that other unknown impurities which carry a quadrupole moment are present in our sample, which would perhaps modify the conclusion drawn above. Further experiments have to settle this interesting question.

During the course of these experiments we discovered another interesting effect which is also related to the quadrupole splitting of the tunneling levels. The variation of the delay time at constant magnetic field allows one to study the decay of the phase coherence of the tunneling systems. In general, in glasses the phase coherence of the tunneling systems is lost due to interaction with thermal phonons and thermally fluctuating neighboring tunneling states. The latter process, which is called spectral diffusion, is known to dominate the dephasing [22]. Independent of the processes that lead to the loss of phase coherence, the amplitude of the echo as a function of the delay time should always decrease monotonically. Figure 3 shows that surprisingly this is not the case for fully deuterated glycerol at zero magnetic field. At short delay times the monotonous echo decay is superimposed by an oscillation. This is clearly not the case for fully deuterated glycerol at high fields and for ordinary glycerol as shown in Fig. 3. Furthermore it is interesting to note that the echo amplitude of fully deuterated glycerol at $B = 0$ is always smaller or at best equal to the corresponding data at $B = 46$ mT. The same statement holds for the comparison of the echo amplitude of fully deuterated glycerol at $B = 0$ with the data on ordinary glycerol taken under the same conditions.

The modulation period of the echo amplitude is about 6.5 μs. The amplitude of the modulation vanishes for long decay times. This modulation effect originates from the level structure exhibited by the tunneling systems of deuterated molecules. The presence of the quadrupole splitting of the tunneling levels leads to a quantum beating in the intermediate state because for such a level scheme, the time evolution of the intermediated state is not described by a single frequency. The effect disappears at high magnetic fields because one is back to the simple

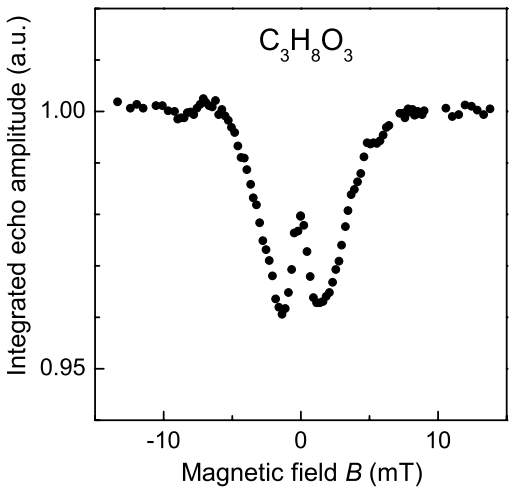

FIG. 2. Integrated amplitude of spontaneous echoes generated ordinary glycerol as a function of magnetic field. The data have been taken at 13 mK.

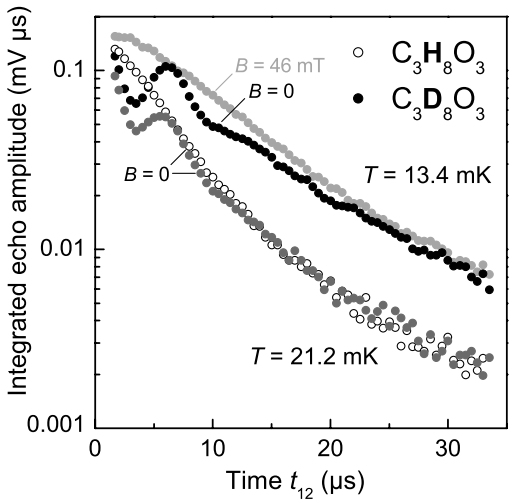

FIG. 3. Integrated amplitude of spontaneous echoes generated in fully deuterated glycerol and ordinary glycerol as a function of the delay time t_{12} and at different magnetic fields. The data at $B = 46$ and the corresponding data at $B = 0$ have been taken at 13.4 mK and the other two sets of data have been taken at 21.2 mK.

situation of two-level systems. For each system only levels with the same nuclear spin state contribute to the echo. In this case no quantum beating is expected.

The period of the oscillation reflects directly the mean quadrupole splitting. From the data shown in Fig. 3 we derive a mean quadrupole splitting of about 150 kHz corresponding to about 7.6 μK. This value is in fair agreement with NMR measurements of the quadrupole splitting in glycerol [21]. For comparison, the energy splitting of tunneling systems in resonance with the external microwave field ($\nu = 1$ GHz) contributing to the echo is about 50 mK. The decay of the oscillation reflects the distribution of the quadrupole splittings involved in the tunneling systems. The asymmetry parameter η of the electric field gradient for deuterium bound to carbon and oxygen has been determined by NMR experiments to be smaller than 0.02 and approximately 0.1, respectively [21]. This corresponds roughly to the distribution of quadrupole splittings needed to explain the decay of the quantum beating in our experiment.

We wish to mention here that quantum beating is known to occur also in NMR experiments with nuclei carrying a nuclear quadrupole moment. Here the external magnetic field leads to the mixing of the states and thus to the modulation of the echo amplitude (see, for example, [23]).

The experiments discussed above do not only show that quadrupole moments play a crucial role in the magnetic field dependence of the dielectric properties of glasses, but also show that very detailed microscopic information can be obtained. Echo experiments in magnetic field on materials with nuclei carrying a well-defined quadrupole moment might help to solve the long-standing question of the microscopic nature of tunneling systems in glassy materials. Selective doping of glycerol with deuterium at the oxygen or carbon site is only one possibility to investigate this question.

In summary, we have performed polarization echo experiments on fully deuterated and ordinary glycerol in magnetic fields to investigate the role of the nuclear quadrupole moment in the unexpected magnetic field dependence of the dielectric properties of glasses at low temperatures. The absence of a magnetic field dependence of the echo amplitude in ordinary glycerol proves the crucial role of the quadrupole moment. In addition, we have observed a new effect in the decay of spontaneous echoes of the fully deuterated glycerol in zero magnetic field. This new effect is an oscillation of the echo amplitude that is superimposed onto the normal decay curve. The origin of this oscillation is a quantum beating with a period corresponding to the quadrupole splitting in this material.

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