Impact of nuclear dipoles on polarization echoes in glasses

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Abstract. A few years ago surprising magnetic field effects were found in non-magnetic glasses at low temperatures (≈ 10 mK). It has since been established that this effect can be attributed to the tunnelling motion of particles carrying nuclear quadrupole moments. The magnetic field effect saturates when the nuclear Zeeman energy becomes larger than the quadrupole splitting. For glycerol this saturation field is around 60 mT. Recently we have observed an additional magnetic field effect which saturates at about 10 times smaller field. This novel phenomenon was studied systematically with 2-pulse dielectric polarization echoes on a series of glycerol samples with different degrees of deuteration. These experiments clearly demonstrate that it originates from the interaction between magnetic dipole moments, giving rise to an energy splitting of approximately 30 kHz. The impact of the nuclear dipoles becomes visible in a quantum beating at zero field and a magnetic field dependence of the echo amplitude. Numerical calculations were performed and compared to the experimental results, shedding light on the microscopic nature of tunnelling systems in glasses.

1. Introduction
The low temperature properties of amorphous solids are governed by atomic tunneling systems (for a review see [1]). Although this is known since over 30 years a detailed microscopic picture of the tunneling motion of atoms or groups of atoms in glasses is still lacking. In the absence of a model based on a microscopic understanding, a phenomenological approach, the so-called tunneling model [2, 3], is used to describe the low temperature properties of glasses. It assumes that the tunneling systems can be described as particles moving in double well potentials having an energy splitting $E = \sqrt{\Delta_0^2 + \Delta^2}$, where $\Delta_0$ denotes the tunneling splitting and $\Delta$ the asymmetry energy arising from a difference of depth of the two wells. Due to the structural disorder of glasses the parameters of these two-level systems are assumed to be broadly distributed.

A new chapter in the low temperature physics of glasses was opened when surprising magnetic field effects in the dielectric properties of glasses were observed in low frequency measurements of the dielectric constant [4] and polarization echo experiments [5]. The origin of the magnetic field effects are tunneling systems containing atoms with nuclear spins [6]. Although the nuclear spin lattice relaxation time is extremely long for dielectric glasses, nuclear spins can influence the properties of tunneling systems, because the tunneling motion can lead to a mixing of different nuclear spin states as discussed below. In turn these tunneling systems cannot be considered as two-level systems anymore due to the fine splitting of each of the two levels caused
by the nuclear spins. Such a mixing has clearly been demonstrated for atoms having nuclear quadrupole moments [7]. Here we show that the nuclear magnetic dipole-dipole interaction gives rise to a similar effect. We have studied tunneling states in partially deuterated glycerol using polarization echoes. In particular we have investigated amorphous glycerol with five deuterons, all bound to carbon atoms. We will refer to this sample as glycerol-d5. The polarization echoes are generated by two short microwave pulses (1 GHz) separated by a delay time $\tau_{12}$ of the order of 10 $\mu$s. Tunneling systems in resonance with the microwave field produce a macroscopic polarization at a time $2\tau_{12}$ after the first pulse as long as phase disturbing processes can be neglected. We will show that the influence of nuclear spins in such experiments can be used to obtain information on the microscopic nature of tunneling systems.

2. The effect of nuclear spins

Selective deuteration allows to place nuclear quadrupoles at specific sites of glycerol molecules. Deuterons have nuclear spin $I = 1$ and carry a quadrupole moment which interacts with the local electric field gradient giving rise to a splitting of the nuclear spin states proportional to the electric field gradient (EFG). If deuterons participate in a tunneling motion in which the glycerol molecule is rotated about some axis, there will be a mixing of their nuclear spin states due to the tunneling process, because the rotation changes the orientation of the EFG with respect to the quadrupole moment. In this situation the tunneling levels experience a fine splitting corresponding to the nuclear quadrupole splitting. Due to the degeneracy of the nuclear spin states the level structure of tunneling systems with one deuteron would be a four-level system.

In a two-pulse polarization echo the polarization after the second pulse is constructed by a combination of all levels that are mixed by the high frequency electric field pulses. Interference between the contributing levels leads to a modulation of the echo amplitude as a function of the delay time $\tau_{12}$. This effect is called quantum beating of the echo amplitude. In particular, for glycerol-d5 we expect a quantum beating of the echo amplitude with a period corresponding to the quadrupole splitting. This effect is best observed at zero magnetic field. In finite magnetic fields the Zeeman interaction causes additional splittings and shifts of the energy levels. Consequently, the interference will change with the magnitude of the magnetic field. In addition, with increasing magnetic field the mixing of the nuclear spin states due to tunneling vanishes. Therefore, for sufficiently large fields the quantum beating disappears and the echo amplitude recovers to the one expected for a simple two-level system. This so-called saturation field for the quadrupole effect in glycerol-d5 is roughly 60 mT.

This quadrupole effect is, however, not the only possible way to mix the nuclear spin states by tunneling. A similar effect arises from the anisotropy of the nuclear dipole-dipole interaction. One can picture this in the following way: During a fast rotation of the glycerol molecule the orientation of the nuclear spins remains fixed in space, whereas the vector connecting the two spins will rotate with the molecule, resulting in a change of the dipole-dipole energy and, even more important, in a mixing of the nuclear states. The dipole-dipole interaction can be described for $n$ dipoles, with distance $r$ and magnetic moment $\vec{\mu}_j = \gamma_j \hbar \vec{I}_j$ by the Hamiltonian

$$H_d = \frac{1}{2} \sum_{i=1}^{n} \sum_{j=1}^{n} \left[ \frac{\vec{\mu}_j \cdot \vec{\mu}_k}{r_{jk}^3} - \frac{3(\vec{\mu}_j \cdot \vec{r}_{jk})(\vec{\mu}_k \cdot \vec{r}_{jk})}{r_{jk}^5} \right]$$

Clearly, this dipole-dipole effect is qualitatively different from the quadrupole effect, because here more than one nuclear moment is involved. While the quadrupole effect factorizes when several deuterons are located on one glycerol molecule, because the quadrupole moments can be considered as independent from each other, the dipole-dipole effect will not factorize.

Due to the fact that the nuclear dipole moment of hydrogen is about six times larger than that of a deuteron we will assume for our discussion that only the dipole dipole effect caused
by the hydrogen atoms will be relevant. Compared to the quadrupole effect we expect a much smaller saturation field of about 5 mT. Also the quantum beating due to the dipole-dipole effect will be on a much longer time scale.

3. Modeling the effect
To describe the experimental results, numerical calculations were performed based on a simple microscopic model. We consider rotational tunneling of one rigid glycerol-d5 molecule with a tunneling angle Θ. Modeling the dipole-dipole effect we have assumed a specific configuration of the three hydrogen atoms on the tunneling molecule and on neighboring molecules. The relative position and distances of the hydrogen atoms on the tunneling molecule are depicted in Fig. 1(a). The configuration of this molecule in the two localized positions between which tunneling occurs, together with three fixed neighboring hydrogens, is shown in Fig. 1(b).

Figure 1. (a) Assumed configuration of H atoms in Glycerol-d5 molecules. (b) The two equilibrium positions of the three hydrogen atoms on the tunneling molecule surrounded by three fixed neighboring hydrogens.

In the numerical calculation we included the tunneling process, the quadrupole effect, the dipole dipole effect and the Zeeman effect in finite electric fields. In our calculations the total hamiltonian for a specific microscopic configuration is constructed automatically, giving us flexibility to model very different situations. The electric field of the rf-pulses is treated as a quantum mechanical perturbation in the limit of small fields. Having obtained the eigenstates $E_{i,1}$ and $E_{j,2}$ of the tunneling system in the groundstate-multiplett and the excited multiplett, respectively, as well as the transition matrix elements $t_{ij}^{(12)}$, the echo amplitude results in [9]

$$A(t = 2\tau_{12}) \propto \sum_{i,k} e^{i(E_{i,1} - E_{k,1})\tau_{12}} \left| \sum_{j} t_{ij}^{(12)} t_{kj}^{*\dagger(12)} e^{iE_{j,1}\tau_{12}} \right|^2 (\Omega_R t_p/2)^4$$

(2)

Here $\Omega_R$ denotes the Rabi frequency and $t_p$ the duration of the microwave pulses.

4. Results
The experimental results of polarization echoes observed in glycerol-d5 are shown in Figure 2. The relative echo amplitude plotted in Figure 2(a) is obtained by dividing the measured echo amplitude in zero magnetic field by the one in high magnetic fields. In this way the decay of
the echo amplitude due to phase disturbing processes is removed and only the quantum beating should remain. Clearly, there is a strong quantum beating effect visible. Figure 2(b) shows the magnetic field dependence of the echo amplitude. The blue dashed line shows the result of a numeric calculation assuming only the quadrupole effect and a tunneling angle of 15°. At fields above 5 mT this model describes the data quite well. Below this field the dipole-dipole effect dominates. Taking the tunneling angle obtained from modeling the quadrupole effect, we can refine our microscopic picture by including the dipole-dipole effect. As mentioned, this effect is very sensitive to the number of dipoles on the tunneling molecule and in its surrounding and the relative motion of the molecule with respect to neighbours.

For glycerol-d₅, we find a good agreement with the experiment for the dipole configuration shown in Figure 1 (the corresponding distances to the neighbors are: 1.9 Å, 1.9 Å and 2.3 Å, respectively). We have assumed in-plane rotation of the three hydrogen atoms on the tunneling molecule. The results of these calculations are shown in comparison with experimental data in Figure 2(a) and Figure 2(b) indicated by the red line. Although the situation in a glass sample is certainly much more complex, the measured effects could be reproduced quite well with this simple model, indicating that a microscopic picture, where mostly one single molecule rotates by about 15°, might represent a typical tunneling system in glycerol.

References

[1] Hunklinger S and Enss C 2000 Insulating and Semiconducting Glasses ed P Boolchand, Series of Directions in Condensed Matter Physics (World Scientific 2000) 17 499
[2] Anderson P W, Halperin B I and Varma C M 1972 Philos. Mag. 25 1
[3] Phillips W A 1972 J. Low Temp. Phys. 7 351
[4] Strehlow P, Enss C and Hunklinger S 1998 Phys. Rev. Lett. 80 5361
[5] Ludwig S, Enss C, Hunklinger S and Strehlow P 2002 Phys. Rev. Lett. 88 075501
[6] Würger A, Fleischmann A and Enss C 2002 Phys. Rev. Lett. 89 237601
[7] Nagel P, Fleischmann A, Enss C and Hunklinger S 2004 Phys. Rev. Lett. 92 24551
[8] Würger A 2004 J. Low Temp. Phys. 137 143
[9] Parshin D 2004 J. Low Temp. Phys. 137 233