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Communication

Capacitor-based detection of nuclear magnetization: Nuclear quadrupole resonance of surfaces

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ABSTRACT

We demonstrate excitation and detection of nuclear magnetization in a nuclear quadrupole resonance (NQR) experiment with a parallel plate capacitor, where the sample is located between the two capacitor plates and not in a coil as usually. While the sensitivity of this capacitor-based detection is found lower compared to an optimal coil-based detection of the same amount of sample, it becomes comparable in the case of very thin samples and even advantageous in the proximity of conducting bodies. This capacitor-based setup may find its application in acquisition of NQR signals from the surface layers on conducting bodies or in a portable tightly integrated nuclear magnetic resonance sensor.

1. Introduction

Wire-wound coils are the most common elements for the creation of localized RF magnetic fields in a number of applications. They are easy to build and optimize for a variety of geometries. However, coil efficiency to create large magnetic fields diminishes substantially in the immediate neighborhood of conducting bodies due to the generation of unwanted eddy currents. For techniques such as nuclear magnetic resonance (NMR) and nuclear quadrupole resonance (NQR), where the coil is the principal detection element, this usually implies an inefficient observation of bulk metals [1–3]. Often the sensitivity can be improved by changing the sample form from bulk to either powders or rolls of very thin foils. Similarly, NMR/NQR suffers in the observation of protecting surfaces of metallic objects, e.g. anti-corrosion layers, anti-abrasive coatings, and other functional layers [4].

Here we propose an NMR/NQR detection technique for the observation of such surfaces employing a capacitor instead of the coil for the excitation and the detection of nuclear magnetization. The capacitor, built here from two copper parallel plates, serves only as a model, whereas the foreseen application is to use a single electrode with a conducting body under investigation forming the other electrode as shown in Fig. 1a. The method presented here should not be confused with an earlier presented method of Prance and Aydin [5], where an electrode was used to indirectly detect coil-excited nuclear magnetization. However, in that particular case, the detection of the associated electric field was substantially modified by the proximity of a tuned coil. A loopless antenna for magnetic resonance imaging was also discussed by Ocali and Atalar [6].

2. Theory

In solids, the observation of nuclear magnetization in the MHz range [7] requires the application of a strong RF magnetic field pulse with a magnitude of ~1 mT at the sample defined frequency (ω) followed by a detection of an extremely small nuclear magnetization ($\mathbf{M}$). Depending on a particular application, this is achieved either by a single coil, or by a separate excitation/detection coil pair [8]. Although the process of detection occurs after the excitation, the two processes are related by the antenna reciprocity theorem [9–11]; the coil's sensitivity for the detection of $\mathbf{M}$ is proportional to the magnetic field produced by the same coil per unit current. This is why the goal of a sensitive coil (probe) is to create as high magnetic field as possible. For a coil adjacent to a conducting body this becomes very difficult, as the induced eddy currents oppose the coil's original magnetic field and therefore lower the final sensitivity. The reduction of the excitation magnetic field can be rather easily compensated by the increase of the

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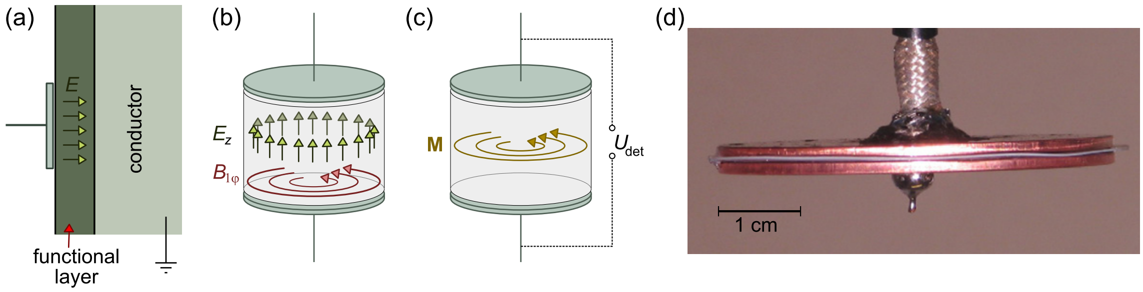

Fig. 1. Observation of nuclear magnetization with a capacitor-based setup: (a) single electrode application, (b) a model parallel plate capacitor during excitation, and (c) during detection. (d) A parallel plate capacitor with cylindrical symmetry and connected with a coaxial cable.

current through the coil during excitation, i.e. by using more RF power. On the other hand, a poor detection sensitivity is primarily overcome by signal averaging techniques, at the expense of the measuring time. A solution to the above issue can be found by noting the fact that the origin of the problem is in a component of the RF magnetic field perpendicular to the surface of the conducting body where eddy currents are induced. It is therefore natural to seek a setup where the RF magnetic field is not perpendicular to the conductive object's surface. A setup which satisfies this requirement is a parallel plate capacitor as described here.

Let us consider a parallel plate capacitor with circular plates of radius R spaced distance d apart and filled with a sample whose dielectric constant is ε as shown in Fig. 1b. The leads connecting the electrodes are straight wires joined to the center of the plates, enabling us to use the cylindrical symmetry.

During the excitation period an RF voltage $U_z = U_0\exp(i\omega t)$ of frequency ω and amplitude U_0 applied to the leads creates a homogeneous electric field inside the capacitor $E_z = E_0\exp(i\omega t)$ pointing in the axial (z) direction. Then, according to the Maxwell equation $\nabla \times \mathbf{H} = \mathbf{j} + \dot{\mathbf{D}}$, the required excitation magnetic field ($\mathbf{B}_1$) inside the capacitor is circular (see Fig. 1b) with a radial (r) dependence of its magnitude

$$B_{1\varphi} = \frac{\pi}{c_0}\frac{r}{\lambda}\frac{U_0}{d}, \tag{1}$$

where the RF wavelength $\lambda = 2\pi/(c_0\omega)$ is determined by the sample defined NQR frequency ω. The value of $B_{1\varphi}$ reaches a maximum of $(\pi/c_0)(R/\lambda)(U_0/d)$ at the capacitor plates perimeter. But this magnetic field is usually neglected in the capacitor, as typically λ are much larger than capacitor dimensions and make R/λ very small. However, the application of a high voltage on a thin capacitor (very small d) can result in large enough $B_{1\varphi}$ to excite appreciable $\mathbf{M}$.

In NQR of powdered samples, the excited $\mathbf{M}$ is linearly polarized along $\mathbf{B}_1$ [12], as shown in Fig. 1b and c. During the detection period, the precession of $\mathbf{M}$ induces a small voltage U_{det} on the capacitor which is the measured quantity. We calculated U_{det} by a lengthy calculation using Maxwell's equations, but the identical result can be derived much easier by simply using the principle of reciprocity [11,9]

$$U_{det} = \omega \int_V \left(\mathbf{M} \cdot \frac{\mathbf{B}_1}{I}\right) dV, \tag{2}$$

where the integral goes over the entire sample volume (V). The quantity $\mathbf{B}_1/I$ is a property of the probe, where $\mathbf{B}_1$ is the magnetic field in the capacitor which would be produced by a current I. To roughly estimate U_{det} with Eq. (2) we assume a simple distribution of $\mathbf{M}$, which is circular and of a fixed magnitude throughout the sample, to obtain

$$U_{det} = \frac{1}{3}\mu_0\omega dR|\mathbf{M}|. \tag{3}$$

In comparison, the corresponding voltage for the usual coil-based detection with a solenoid of radius R_{coil} and N turns is $\pi\mu_0\omega NR_{coil}^2|\mathbf{M}|$, typically a much larger value.

3. Experimental

To experimentally verify the feasibility of the proposed approach, we selected ^{35}Cl NQR of $NaClO_3$. The crystallographic structure of $NaClO_3$ implies a single ^{35}Cl NQR transition which is found at $\nu_0 = \omega/(2\pi) = 29.92$ MHz at room temperature and therefore the associated $\lambda = 1.75$ m (a dielectric constant $\epsilon = 5.7$ was used). Our probe, the capacitor, was built from two Cu circular plates of a diameter $2R = 4.6$ cm and a $d = 500$ μm thick teflon ring as a spacer. The space between the capacitor plates was filled with ~1.5 g of $NaClO_3$ powder, mixed with a small amount of silica paste to prevent piezoelectric ringing, and glued together. We used two configurations of the capacitor leads. In the first, leads were approaching the capacitor from the opposite sides as shown in Fig. 1b. In this configuration, the magnetic field extends also outside of the capacitor and is therefore more susceptible to external noise. In the second configuration, a coaxial cable was used for the two leads, with the coax core going through one of the plates as shown in Fig. 1d. The advantage of this setup is a fully confined magnetic field within the capacitor. Each of the so prepared probes was then tuned to ν_0 with a coil in parallel and embedded in our conventional 50 Ω setup [13] through a passive switch: transmitter channel to the power RF amplifier and receiver channel to a low noise preamplifier. Special care was also taken to prevent any coupling between the tuning coil and the sample.

4. Results and discussion

The signal obtained with this capacitor-based probe is shown in Fig. 2a. Here, 50,000 acquisitions were averaged to reduce the noise level. The signal was excited with the solid-echo pulse sequence, $90_x - \tau - 90_y - \tau$, with $\tau = 100$ μs and close to the resonance frequency. The signal obtained with a single pulse sequence (not shown) was significantly stronger, but was contaminated with probe ringdown response. In addition, some remaining instrumental artefacts were also removed by a phase cycled average of eight consecutive responses. A minor complication which also occurred was the shifting of the resonance frequency due to RF heating of the sample, which is a well known problem in NQR. At a repetition time of 50 ms the resonance line shifted by more than 10 kHz. This shift was quickly reduced when the repetition time was increased and completely vanished at a repetition time around 1 s. The pulse length t_{90° yielding maximum signal was approximately 100 μs when using 300 W RF power amplifier.

Although the observed signal in Fig. 2a was rather weak, satisfactory agreement between several predicted and experimentally determined parameters was found. The theoretical value of the

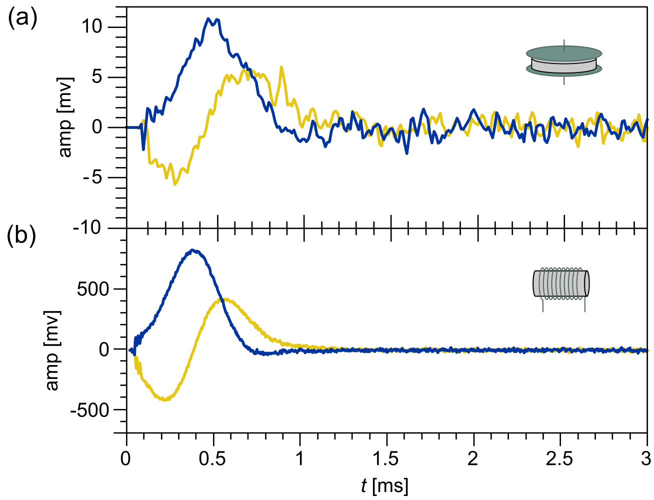

Fig. 2. ^{35}Cl NQR signal of 1.5 g $NaClO_3$ at 29.9 MHz in two sample geometries as obtained with a solid-echo pulse sequence: (a) sample in the capacitor and (b) sample in the coil.

average excitation magnetic field $\overline{B}_{90^\circ} = 0.6$ mT yielding the best signal was found from the expression $\gamma\overline{B}_{90^\circ} t_{90^\circ} \approx \frac{1}{4}$, where $\gamma = 2.62 \cdot 10^7$ rad/(sT) for ^{35}Cl. On the other hand, $\overline{B}_{90^\circ} = 0.385$ mT was estimated from Eq. (1) and from the measured voltage on the capacitor $U_{exc} \sim 1.4$ kV (corresponding to $E_0 = 2.8$ MV/m). The two values are in reasonable agreement. The second comparison is that of U_{det}. An approximate theoretical value $U_{det} = 28$ nV is obtained from Eq. (3) and the expression for spin 3/2 NQR echo magnetization of a single crystal [12, p. 74] $|\mathbf{M}| = 0.281 n N_A \frac{h\nu_0}{kT} \hbar\gamma = 40 \times 10^{-6}$ A/m (magnetic field is ~50 pT). Here N_A is Avogadro's number and $n = 0.023$ mol/cm^3 for $NaClO_3$. On the other hand, $U_{det} \sim 7$ nV was determined from the acquired amplified signal amplitude 12 mV, as shown in Fig. 2a, and reduced by the overall gain of our spectrometer (124.3 dB). This value of U_{det} is a factor of four smaller than predicted, however, our theoretical estimate of 28 nV, must be reduced by ~1/2 to account for random orientations in a powder and by an additional numerical factor due to a suboptimal excitation. Taking these factors into account, again satisfactory agreement is achieved.

A signal of the same amount of $NaClO_3$ was also obtained with a conventional coil-based setup and is shown in Fig. 2b. We have here made 1000 averages and used the same solid-echo pulse sequence with 5 μs pulse lengths. The sample was prepared by pressing the $NaClO_3$ powder in a tube 10 mm long and 10 mm in diameter. A coil of four turns was wound directly on the tube. A comparison of the capacitor-based signal (Fig. 2a) and the coil-based signal (Fig. 2b) reveals, that the capacitor-based detection results in a much smaller S/N, although the same amount of sample was used. However, there are two factors which prevent a direct comparison: (i) the sample geometry is different in the two experiments and (ii) the performance of the acquisition circuitry is also different. For a fixed amount (volume) of sample, the coil giving maximum S/N is obtained when coil's diameter and length are approximately equal, the space between the turns is equal to the wire diameter and the filling factor is very high [13]. Therefore, the S/N as seen in Fig. 2b is the most favorable for any coil-based detection. For a thin sample, like the one used in our capacitor-based detection, the above coil geometry would require a huge coil and give a poor S/N due to a small filling factor. In such cases, other coil geometries with better performance are used, but the S/N of optimally shaped sample is only partially recovered.

The main source of noise in a coil-based NQR, or solid state NMR, is usually due to the resistance of the pickup coil, whereas the noise of other components, including the tuning capacitor, can be practically neglected. In our capacitor-based setup however, the noise of other components cannot be neglected, as these include a tuning coil connected in parallel with the pickup capacitor. In general, the reason for tuning the pickup element is to increase the overall response at the preamplifier input, but unfortunately in our case this also introduces a large source of noise and thus significantly decreases the observed S/N as shown in Fig. 2a. One possibility to decrease this noise is by decreasing coil's temperature, e.g. submerging the tuning coil in liquid nitrogen. Theoretically, however, we can exclude this noise completely, and an interesting comparison of capacitor versus coil results. We have made several numerical estimates of the intrinsic signal voltage and Johnson's noise when detecting a thin disc-like sample of dimensions similar to the one used in our experiments for two cases: (i) an isolated thin capacitor (no tuning coil) and (ii) an isolated single loop coil representing a typical surface coil (no tuning capacitor). In general, we find that the signal voltage on the thin capacitor is always smaller than the corresponding voltage on a single loop coil. However, the same is also true for the Johnson's noise, as capacitor plates resistance is smaller than the wire resistance of the single loop coil. The corresponding S/N ratio is surprisingly comparable for both cases.

Our main interest is however a thin sample on a conducting surface. Including this surface in the above calculations does not change the capacitor S/N as one electrode can be simply replaced by the conducting surface. However, the conducting surface has a dramatic effect on a single loop coil when they are coplanar. First an additional resistance is introduced due to the induced eddy currents and thus the overall noise is increased. And second, eddy currents also substantially decrease the coil's sensitivity (B_1/I) and therefore the signal voltage. Both contributions decrease the overall S/N thus making the thin capacitor setup more advantageous.

We have here demonstrated an NQR excitation/detection setup. However, equivalent experiments could be performed also with nuclear magnetic resonance (NMR). Here, the requirement for a homogeneous static and RF magnetic fields probably excludes the possibility of high resolution measurements. On the other hand, magnetic capacitor plates would be an interesting idea for a tightly integrated low resolution NMR sensor.

5. Conclusions

In conclusion, we have shown that the precession of nuclear magnetization can be excited and detected by a capacitor. Whereas for NQR of bulk samples, the S/N of a capacitor-based setup is much lower compared to the S/N of a conventional coil-based detection, the capacitor-based setup offers potential advantages for the NQR detection of thin samples near or on conducting bodies.

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