

Pulsed EPR with Field Cycling and a Bridged Loop–Gap Resonator Made by Chemical Deposition of Silver

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This paper describes the measurement of the zero-field electron spin–lattice relaxation time of a coal sample by pulsed EPR under field-cycling conditions. The detection system uses an inexpensive homebuilt bridged loop–gap resonator made by chemical deposition of silver. © 1997 Academic Press

INTRODUCTION

EPR and ENDOR spectra in powder samples show inhomogeneous line broadening due to the magnetic inequivalence of otherwise identical spins. Zero-field resonance [ZFR (1)] removes this disadvantage but is limited to the case of high hyperfine fields or appropriate zero-field splittings. However, if one performs the excitation of transitions in zero magnetic field and the detection in a high field, the resolution of ZFR and the high sensitivity of EPR are combined. An experiment of this kind called *field-cycled* ENDOR has recently been described (2). Field-cycling experiments have been known in nuclear-quadrupole double-resonance spectroscopy for a long time [*level crossing*, DRLC (3)]. Because of their high gyromagnetic ratio, protons are usually used in DRLC as the detector of zero-field interactions of other nuclei.

In a field-cycled ENDOR experiment, electrons play a similar role to that of the protons in DRLC. An important difference between the two experiments as seen from an experimental point of view is the order of magnitude of the spin–lattice relaxation time for protons (T_{1n}) and for electrons (T_{1e}). This may be hours for protons and only a few milliseconds for electrons at 4.2 K. The spin system must be demagnetized adiabatically in a field-cycling experiment. This means, on the one hand, that the cycling must be slow enough to avoid excitation of transitions during the cycle. On the other hand, the complete cycle must be carried out within a period of time shorter than the spin–lattice relaxation time in order to prevent energy exchange between the spin system and the lattice. The first condition is easily satisfied for electrons, but the second condition can only be met by using rapidly switched air-core magnets (4), e.g., as

in our field-cycling spectrometer (5) which can be switched from 0.33 T to zero and back, each within 0.5 ms.

In this paper, we describe the measurement of the zero-field electron spin–lattice relaxation time (T_{1De}) of a coal sample by pulsed EPR under field-cycling conditions. An inexpensive homebuilt bridged loop–gap resonator (BLGR) is used for the detection. We describe here for the first time how a BLGR is made by chemical deposition of silver on a precision EPR quartz tube.

EXPERIMENTAL

Resonator Design

The BLGR was introduced to EPR by Forrer and Pfenninger (6, 7). Handmade X-band resonators of this kind were described by Forrer *et al.* (8) and by Crepeau *et al.* (9). These groups used conducting gold or silver paint for the metal parts of the resonator. As we reported in a preliminary paper (10), resonators of this type can very easily be made by chemical deposition of silver on quartz glass in an aqueous solution using potassium sodium tartrate as reducing agent. The resonator structure can be obtained after the deposition by scratching or during the deposition by a mask (Fig. 1) which covers all parts of the glass which are to form the resonator slots.

Precision EPR quartz tubes (Wilma Glass Co., Buena, New Jersey 08310) with a tolerance of ± 0.013 mm were used in order to fit the mask precisely into the resonator. The quartz glass must be carefully cleaned before the chemical deposition. This pretreatment of the quartz surface is the crucial step in the deposition. The tubes were kept overnight in a 1:1 mixture of 30% hydrogen peroxide and concentrated sulfuric acid. The tubes can be manipulated in this solution with the aid of Pasteur pipettes. Further cleaning was done with a large amount of 2 N sodium hydroxide solution, distilled water, and a 2% solution of SnCl_2 in water. The tubes which must not be touched by hand after this cleaning were then carefully washed with distilled water.

Two solutions were prepared for the deposition: The first

solution consisted of 0.2 g potassium sodium tartrate in 50 ml water, the second solution of 0.5 g silver nitrate in 25 ml water to which just as much 2 *N* ammonia was dropped as was necessary to dissolve the initially formed precipitate. A new polypropylene beaker without scratches was placed in an oil bath which was heated to 60°C and filled with equal amounts of the above two solutions. The quartz tubes were now heated on the tip of a pasteur pipette for 1 min with a hairdryer, and then placed in the silver solution where they were left for approximately 3 hours, and then carefully washed with water. A mask of Delrin (Fig. 1) can be used covering the parts of the resonator which are to form the slots. Alternatively, the slots can be scratched with satisfying accuracy after the deposition with a tool made from a steel rod with the same diameter as the inner diameter of the quartz tube. The bridges on the outside of the tubes were scratched by hand with a sharp knife using stereoscopic

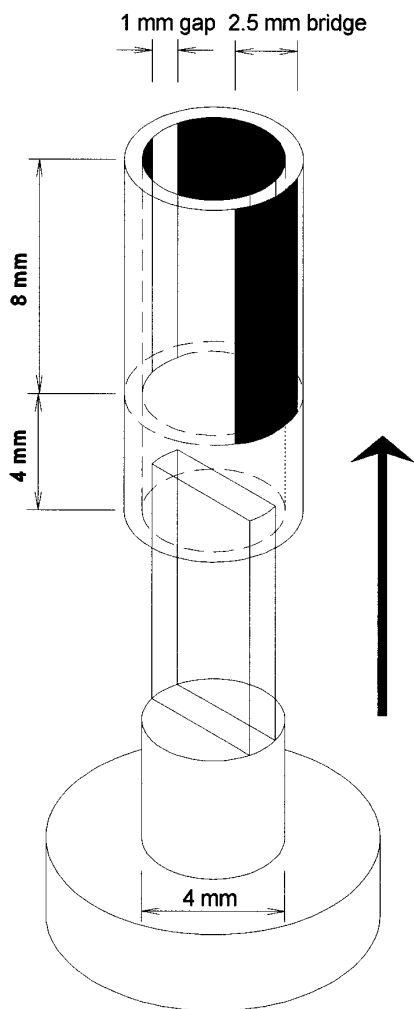


FIG. 1. BLGR (upper half) and the mask (lower half) used during the chemical deposition of silver on a precision EPR quartz glass tube.

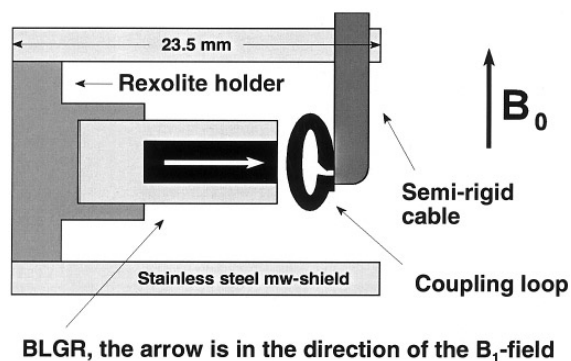


FIG. 2. ESE probehead with BLGR used in the field-cycling experiment.

magnifying lenses. It should be no problem to modify the mask so that the bridges too are formed during the deposition. With the procedure described, BLGRs with a shiny opaque silver surface were obtained.

Details of the Probehead

The use of a liquid-He cryostat, the tail of which must fit into the solenoidal coil, restricts the available experimental space drastically. This fact together with the vertical field direction in a solenoid makes it impossible to use a commercially available ESE (electron-spin-echo) probehead. Our probehead (Fig. 2) has a diameter of only 23.5 mm. Its cylindrical case of stainless steel functions as the microwave shield. A rexolite holder movable within the case supports the BLGR which is aligned perpendicular to the axis of the solenoid. The coupling to the transmission line is checked with a Weinschel 430A sweep oscillator, a Marconi 2440 microwave counter, a Rhode & Schwarz NRVD dual-channel power meter, and a HP 772D dual directional coupler. Impedance matching is achieved at room temperature by moving the rexolite holder in the probehead. We cannot vary the coupling in liquid helium due to the limited space in our cryostat. The voltage-standing-wave ratio changed from 1.05 at room temperature to 1.6 in liquid helium. The *S/N* of a coal sample increased from 15/1 at room temperature to 80/1 in liquid helium.

RESULTS AND DISCUSSION

Resonator Performance

The measurements of the resonance frequency f_0 and the loaded quality factor Q_L of our resonators were performed with the microwave test-bench equipment mentioned above. The resonance frequency could easily be adjusted between 9 and 10 GHz by reducing the width of the silver strip on the outer surface of the resonator. The quality factor was

determined from $f_0/\Delta f$, where Δf is the 3 dB bandwidth. The Q_L values of our resonators ranged from 200 to 300. An ESE obtained at room temperature with our BLGR resonator in a homemade EPR probehead built for a conventional (not field-cycled) magnet is shown in Fig. 3. The S/N is approximately 40/1. This is comparable to the S/N of the Bruker dielectric resonator, for which we found a S/N of 50/1 under the same experimental conditions. Our resonators were cycled many times between room temperature and liquid nitrogen or liquid helium without problems. We observed no fissures which can occur with BLGRs made by other techniques (11).

Detection Methods in Field-Cycling EPR

The detection of the magnetization in a field-cycled experiment can be started after complete settling of the field, approximately 2 ms after return to the high field in our spectrometer. In their field-cycled ENDOR experiment, Krzystek *et al.* used CW detection which took 50 ms. We measure the magnetization after the cycling by an ESE. As can be seen from Fig. 4, our ESE detection starts immediately after the beginning of the detection period and is finished within 2.5 μs . The pulsed detection is mandatory for substances with relaxation times T_{1e} much shorter than those of the CW experiment of Ref. (2) in which the range of substances suitable for investigation must necessarily be limited for this reason. The T_{1e} time of the coal sample investigated in this paper was 14 ms at 4.2 K in contrast to the T_{1e} times of 1–10 s for the compounds in the paper of Krzystek *et al.*

Detection of the Zero-Field Electron Spin–Lattice Relaxation Time

Variation of the time spent in zero field allows the determination of the zero-field electron spin–lattice relaxation time T_{1De} . Figure 5 shows echoes of a coal sample (impregnating pitch HL, VfT AG Castrop-Rauxel) at high field

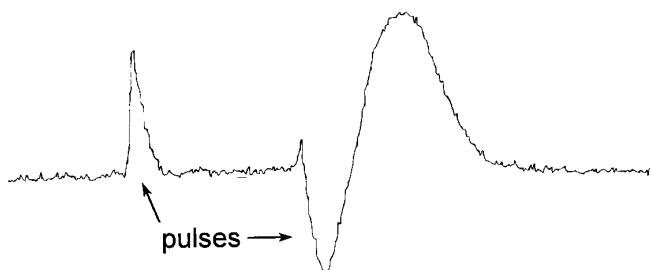


FIG. 3. ESE of impregnating pitch HL at room temperature recorded with the resonator described in this paper and two low-power pulses of 300 ns width with 800 ns pulse interval. Sweep width, 3000 ns. No accumulation.

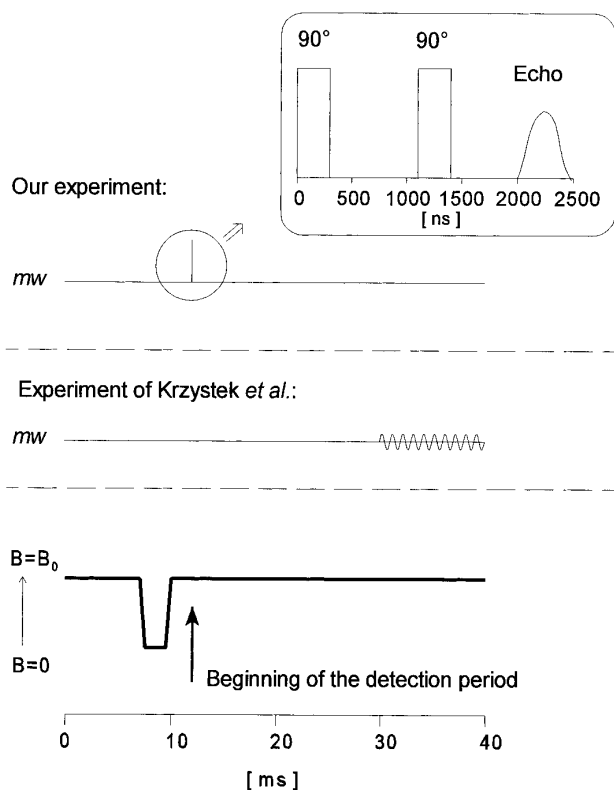


FIG. 4. (Bottom) In our case, and very similarly in the experiment of Krzystek *et al.*, the field cycling consists of 0.5 ms for switching from high field to zero field, a variable delay in zero field, 0.5 ms for switching back to the initial field value, and 2 ms for stabilization of the field. (Center) CW detection of the magnetization, which starts 18 ms after the beginning of the detection period and lasts for 50 ms (not completely drawn) in the experiment of Ref. (2). (Top) Our ESE detection which takes 2.5 μs .

(A), after minimal time in zero-field (B), and after a very long time in zero field (C). The difference between B and C can be used in double-resonance experiments. The echo C is due to magnetization which builds up during the cycling. The inset in Fig. 5 shows the dependence of the integrated echoes on the zero-field dwell time. The T_{1De} time constant of this sample is 1.6 ms at 4.2 K. The order of magnitude of the zero-field relaxation time for this coal sample which may be regarded as a typical organic radical proves that our pulsed detection makes it possible to perform pulsed field-cycled ENDOR experiments on most organic compounds.

CONCLUSION

The measurement of the zero-field electron spin–lattice relaxation time of a coal sample under field-cycling conditions has been presented. The BLGR used in the detection system was made by the inexpensive and very simple way of chemical deposition. The present study shows that a

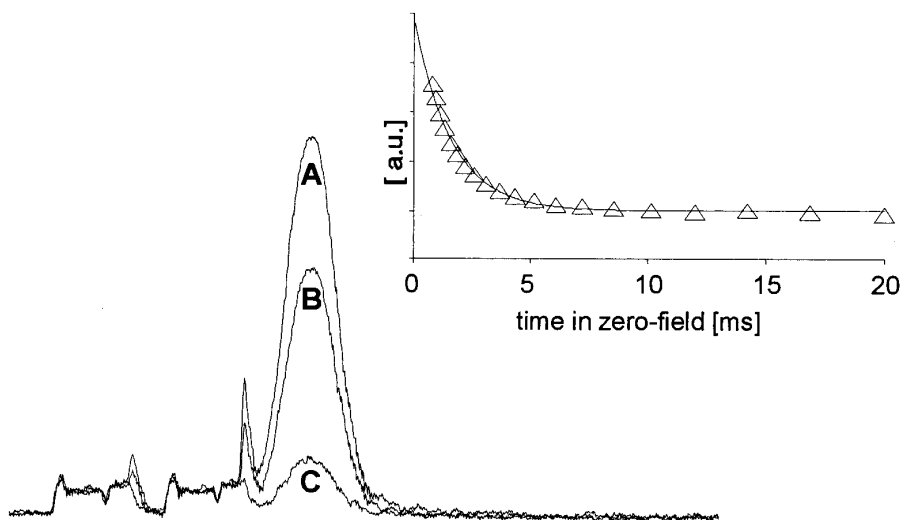


FIG. 5. ESE of impregnating pitch HL at 4.2 K in the X band with two low-power pulses of 300 ns and 10 accumulations. (A) High-field signal, (B) signal after minimal (0.8 ms) time in zero field, (C) signal after 100 ms in zero field. (Inset) Dependence of the integrated echoes on the zero-field dwell time.

pulsed field-cycled ENDOR experiment will be possible with typical organic radicals. It is expected that further studies will yield ENDOR spectra with a resolution that cannot be achieved by other methods.

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