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New Transmission-Line Resonator for Pulsed EPR

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During the past few years, many efforts have been made to develop new resonance structures for EPR applications. The main aim of these is to increase the S/N ratio of the detected signals, especially when working with samples of small volume. Various technical problems, related in particular to the introduction of additional features such as double-resonance RF coils and optical access, also contribute to the complexity of the design problem.

The common trend in the design of resonators with a high filling factor is to use undersized structures with dimensions less than the wavelength. Resonators developed for pulsed EPR such as the loop–gap resonator {LGR} (*1*), the slotted tube resonator {STR} (*2*), and the ''Mims''-type strip line resonator {MSLR} (*3*) and some of its latest modifications (*4, 5*) represent such a quasi-lumped circuit approach. The LGR is used most frequently at frequencies from L to X band. It shows good sensitivity due to its high filling factor combined with a fairly high microwave magnetic field homogeneity. However, for samples with high dielectric losses, the relatively poor separation between the electric and magnetic components of the microwave field causes the actual sensitivity to be strongly reduced. This situation is greatly improved in the so-called bridged loop–gap resonator {BLGR} developed by Pfenniger *et al.* (*6*). The principal problems in loop–gap resonator design occur when ENDOR operation is required. It is difficult to avoid coupling of the RF coils to the microwave field. Therefore, one is forced to place the RF coils outside the resonator, leading to a reduced RF amplitude at the sample location. In contrast, because of its partly open structure, the STR is very suitable for ENDOR applications. For the same reason, optical access is very easy. These advantages must be paid for by a rather poor filling factor. The MSLR combines a very high filling factor with a very low Q value. Originally, it was designed for single-crystal pulsed EPR studies and observation of the linear electric field effect {LEFE} (*7*). Also in this design, RF coils can be easily incorporated (*8*). These advantages are, however, overshadowed by the inconvenient sample handling of powders and solutions.

Searching for possible solutions, our attention has been attracted to the Alderman–Grant resonator {AGR} (*9, 10*). This structure is well studied for radiofrequency applications in high-resolution NMR and MRI. One of the versions of this resonator appeared to be transformable for use in the microwave region (*11*). The original AGR is manufactured from copper or aluminum foil with chip capacitors, and ideologically represents a high-frequency analog of saddle coils (Fig. 1). Two H-shaped foil pieces {1} are bent around a cylindrical former {8}; four chip capacitors {5} are soldered between the wings of the structure to close the current loops. Two metal strips {3} placed under the wings and separated from them by a thin insulating layer {7} act as the ''guards'' preventing the electric fringing fields from penetrating into the sample. The Alderman–Grant resonator is known to have extremely good separation of the electric and magnetic radiofrequency fields (which is usual for devices with all the electric field concentrated in the lumped capacitance). Extensive studies of the AGR geometry have led to an optimal strip-to-window-width ratio of 78°/102° (*10*) which provides the highest homogeneity of the magnetic field inside the structure.

To work in the microwave region, the structure has been scaled down, resulting in a substantial decrease in the strip and wing inductance. The chip capacitors were substituted by bridges like those used in the BLGR (Fig. 2A). The first structures were made of silver foil, but later models were painted on quartz tubes using silver paint. The mw-AGR has three principal resonance frequencies, one corresponding to the principal AGR mode. Two other frequencies correspond to LGR modes with slightly different resonance frequencies; these modes are due to the currents in upper and lower BLGR-like structures (involving circular currents in the wings and bridge capacitors). It is relatively easy to design the structure with these frequencies far apart from each other in order to allow the excitation of the AGR mode without any interference with the BLGR modes. It turned

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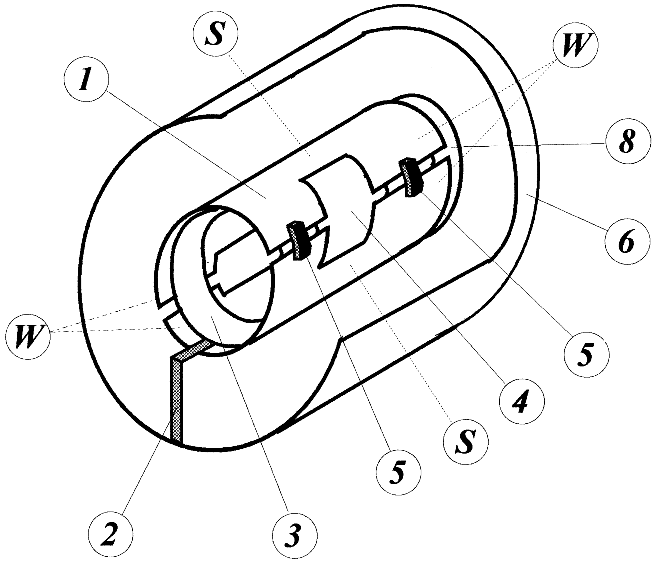

FIG. 1. Basic design of Alderman–Grant resonator for NMR applications (an overall view). {1} H-shaped conductor, {2} grounding strip, {3} conducting ring, {4} window, {5} chip capacitors, {6} radiation shield, {7} isolating layer, {8} coil former, and {W} wings and {S} strip of the H-shaped conductor.

out that the original formulas (*10*) for the resonance frequency of the AGR work satisfactory for the C- and S-band structures. Figure 2B shows the result of simulation of the equiflux line pattern in the transaxial (across the window) cross-section of the AGR.

The first experiments with the microwave AGR structures were conducted in Nijmegen (*11*). A cryogenic insert for the AGR structures has been designed, constructed, and tested for temperatures down to 6 K. The first pilot experiments demonstrated that the AGR had good frequency and coupling tuning stability, i.e., small ''acoustic'' susceptibility, a high filling factor and comparatively high loaded *Q* value (similar to a LGR with same frequency), a good microwave *H*- and *E*-field separation (at least as good as for the BLGR), and a high microwave magnetic field homogeneity in the working volume.

The vertical cylindrical shape of the resonator allows convenient access of standard EPR sample tubes. At the same time, the B_1 field is orthogonal to the cylinder axis. This makes the structure particularly suitable for use in combination with solenoidal RF coils, enabling very high ENDOR fields. For the same reason, the parallel excitation mode (i.e., $B_1//B_0$) can be realized by simply rotating the magnet or the insert. Finally, the large side windows allow easy optical access.

Preliminary experiments have been carried out on a home-built C/S band ESE spectrometer (*12*) and structures with resonance frequencies in the range from 2.5 to 7.5 GHz. The resonator operating near 4.0 GHz is painted upon the quartz tube with an inner diameter of 5.4 mm and an outer diameter of 6.5 mm. The overall length of the painted structure is 14.6 mm; the length of the window is 8.6 mm. The active volume at $0.7B_{1max}$ level measured via the ESE signal of a small test sample is 6 mm high with a diameter of 5 mm. The loaded quality factor for the foil-based structures is about 500–600, while for the painted structures it is two to three times lower. Comparison of the new resonance structure with the three-loop two-gap LGR, homemade from bulk aluminum (and having the same working volume), has shown that for the same test sample at room temperature, the S/N ratio is up to 30% higher for the foil-based AGR structure. In Fig. 3, a typical ESE spectrum of a standard (Bruker) coal sample recorded at 6 K is presented.

In this Communication, we have demonstrated that the

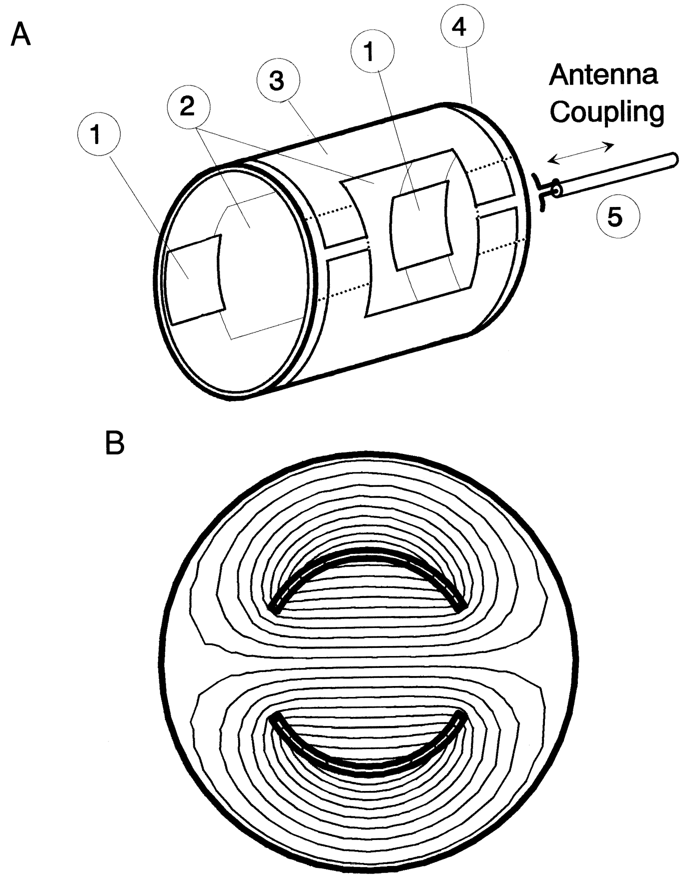

FIG. 2. (A) Alderman–Grant resonator scaled down to work at microwave frequencies. {1} Inner bridge capacitors, {2} windows, {3} H-shaped structures, {4} quartz support tube, and {5} coupling antenna. (B) The equiflux lines (magnetic field direction) pattern in the transaxial cross section of the AGR (across the window in the structure). The resonator geometry is close to the optimal one in terms of the best B_1 homogeneity; the foil of the strips is thinner than the skin depth at the working frequency. Current density is chosen to be uniform through the strip cross section. Simulations are made using software package ''Quickfield'' V3.2 by Temati.

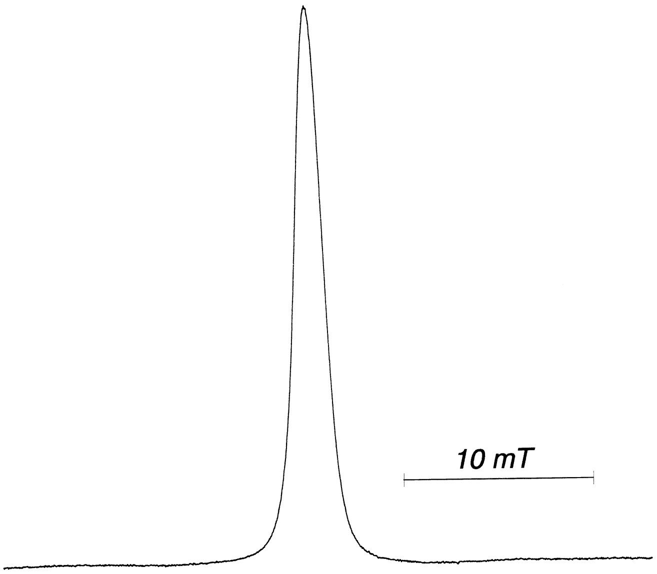

FIG. 3. Echo-induced EPR spectrum of coal (Bruker standard sample) recorded at 5.26 GHz at 6 K with the critically coupled resonator. Other parameters: sweep width, 25 mT; sweep time, 1 min; boxcar averager time constant, 100 μs; two-pulse echo sequence (t_{p1} = 30, t_{p2} = 60, τ = 250 ns); repetition rate, 100 KHz.

concept of ''transforming'' RF resonance structures into the microwave domain is very fruitful. It is to be expected that other structures, such as the so-called ''birdcage'' resonators (*13*), are equally suitable candidates to be ''transformed'' to microwave frequencies. In conclusion, a promising new pulsed EPR resonator structure has been developed. It is anticipated that this design will lead to attractive possibilities to incorporate ENDOR coils. This development as well as modifications ton include frequency-tuning capabilities are currently in progress in our laboratories.

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