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ENDOR spectroscopy at 275 GHz

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Abstract

A pulsed ENDOR spectrometer operating at a microwave frequency of 275 GHz is described. The results demonstrate that this type of spectroscopy can now be performed routinely at this high microwave frequency. The advantages compared to conventional EPR frequencies are the high spectral resolution, time resolution, and sensitivity.

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1. Introduction

The attraction of electron nuclear double resonance (ENDOR) spectroscopy is the possibility to measure unresolved hyperfine interactions in electron paramagnetic resonance (EPR) spectra. The ENDOR spectra not only allow for an identification of the paramagnetic center but also supply detailed information about its electronic structure. In the last decade, the ENDOR technique has seen a remarkable revival owing to the development of high-frequency EPR spectroscopy that started in 1981 with the pioneering work of Lebedev and co-workers [1]. Already in 1988, the first observation of ENDOR at 97 GHz was reported [2] and in this frequency band ENDOR is now a well-established technique [3]. The attractions are that in the related magnetic field of about 3.4 T the high Zeeman frequencies of the various nuclei lead to a high ENDOR sensitivity and moreover to a high spectral resolution. In addition, it proves possible to perform orientationally selective ENDOR in random samples, owing to the anisotropy of the g-tensor. As a result ENDOR spectroscopy at W-band (95–97 GHz) provides information about the electronic structure of paramagnetic species that remains invisible at conventional EPR frequencies.

EPR experiments at W-band are now widely applied and the results have stimulated several groups to continue the development of EPR technology to frequencies around 300 GHz and higher but reports about successful ENDOR spectrometers at these high frequencies are scarce. This is understandable because at these frequencies the construction of single-mode microwave resonators, necessary to obtain a strong microwave B_1 field, requires an extreme mechanical precision. In addition, the requirement to apply a radiofrequency (RF) field to induce the nuclear transitions makes the mechanical construction of the probe head even more demanding.

In this contribution, we present the performance of a pulsed ENDOR spectrometer operating at an EPR frequency as high as 275 GHz. The system is essentially an extension of the EPR spectrometer described recently [4]. The cylindrical, single-mode resonator that allows for pulsed EPR experiments with pulse durations of 100 ns with an incident microwave power of a little more than 1 mW has now been equipped with narrow slits in the walls. These slits permit the RF field B_2, generated in two small RF coils that are positioned in a Helmholtz configuration outside the cavity, to reach the sample. It turns out that this construction works very satisfactorily

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for ENDOR spectroscopy at this high microwave frequency, as we will demonstrate with the help of two examples. The spectrometer allows us to obtain ENDOR spectra over an RF frequency range of several hundreds of MHz employing RF pulses with a duration as short as 5 μs. The results confirm that a sensitivity and resolution is achieved that is superior to that obtained in ENDOR spectra at W-band.

2. Experimental

In Fig. 1 an exploded view is presented of the 275 GHz ENDOR probe head that is located in a helium gas-flow cryostat. It consists of a horizontally positioned TE_{011} cylindrical cavity that contains the sample. This cavity is almost identical to the one presented in our previous paper [4]. The only difference is the set of three slits in the cavity wall to allow the RF magnetic field to reach the sample that is contained in a thin Suprasil tube in the center of the cavity. The slits, cut with the help of a circular saw, have a width of 0.1 mm and the bars separating them have a thickness of 0.1 mm. The metal block (made from bronze) containing the cavity has been adapted to accommodate the 2 two-turn RF coils with a diameter of 3 mm that are connected in series. The distance between the center of the coils and the sample is 3 mm. The B_2 field generated by the current in the coils is perpendicular to the vertically oriented static magnetic field B_0 and the microwave magnetic field B_1. The loaded quality factor of the cavity $Q \approx 1000$ as compared to $Q \approx 1500$ for the cavity without the slits.

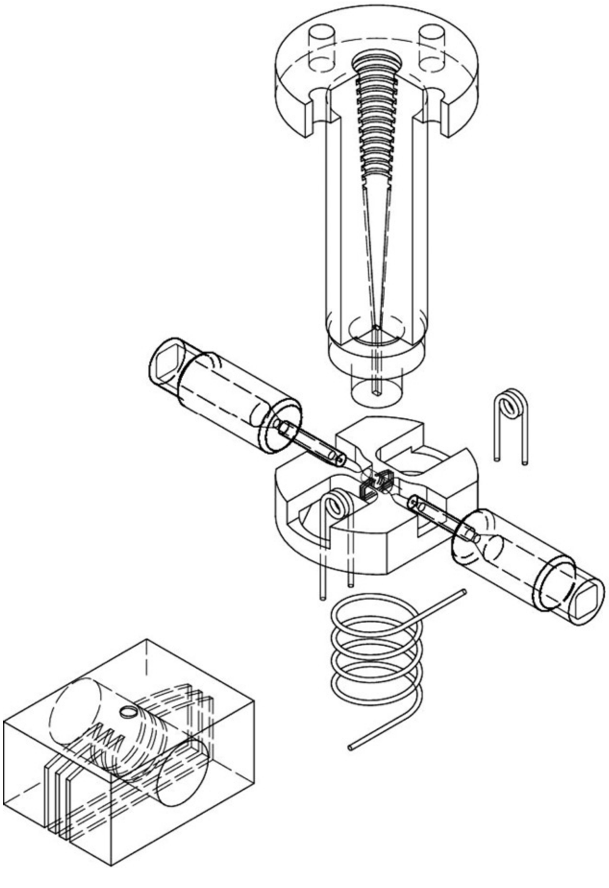

Fig. 1. An exploded view of the probe head of the 275 GHz pulsed EPR/ENDOR spectrometer. The cylindrical resonator is at the center of the bronze block and is shown separately on a larger scale in more detail. The diameter of the resonator is 1.4 mm and its length can be varied between 1.0 and 1.4 mm with two movable plungers to tune the cavity to the fixed frequency of 275.7 GHz of the oscillator. Three slits with a width of 0.1 mm and at a mutual distance of 0.1 mm are cut in the block with the help of a circular saw. Two two-turn RF coils with a diameter of 3 mm are positioned outside the cavity. The unit shown at the top is the taper that serves to change the circular shape of the corrugated waveguide to the rectangular waveguide to optimize the coupling of the microwaves into the cavity. The coil below the cavity block serves to modulate the magnetic field in cw EPR experiments.

RF pulses with a typical pulse duration of 6 μs are generated by a combination of a Rohde & Schwarz type SML 01 frequency synthesizer and an Amplifier Research type 100W1000B RF amplifier with a maximum output of 100 W. The RF pulses are guided to one side of the RF coils via a coaxial cable. A second cable connects the other side of the RF coils with a 50 Ω load located outside the cryostat. The advantages of this structure are its simplicity and the large bandwidth. Since the inductance of the two ENDOR coils is as small as 20 nH, the impedance only starts to reduce the RF current at frequencies higher than 300 MHz.

3. System performance

Two samples were used to test the performance of the 275 GHz ENDOR spectrometer. The first sample is a single crystal of $ZnGeP_2$ doped with 0.2 % Mn^{2+} ions. In Fig. 2 the EPR spectrum of this sample is shown,

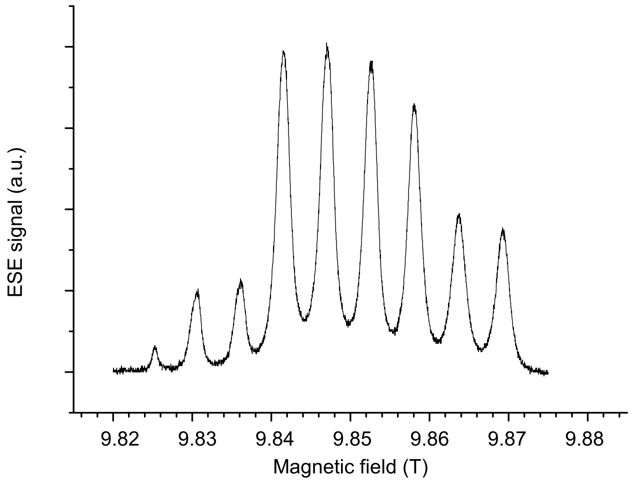

Fig. 2. The stimulated-echo-detected EPR spectrum of the Mn^{2+} ions in a single crystal of $ZnGeP_2$ with the magnetic field perpendicular to the *c*-axis of the hexagonal crystal. The microwave frequency is 275.7 GHz. $T = 10$ K.

as recorded at 10 K with the magnetic field perpendicular to the *c*-axis of this hexagonal crystal. This spectrum is obtained in pulsed mode by detecting the stimulated electron-spin-echo signal following three microwave pulses with a duration of 250 ns. The first two are separated by 1 μs and the second and third by 6 μs. The spectrum exhibits the characteristic structure of the $S = 5/2$ electron spin of the Mn^{2+} ion with an isotropic hyperfine interaction $|A| = 158$ MHz with the $I = 5/2$ nuclear spin of ^{55}Mn. The set of six strong lines correspond to the $m_S = -5/2 \leftrightarrow m_S = -3/2$ transition. This transition dominates the spectrum because of the high Boltzmann factor $\exp\{-\Delta E/kT\} \approx 3.8$ at 275 GHz and 10 K. The three weaker lines at lower field are part of a set of six lines corresponding to the $m_S = -3/2 \leftrightarrow m_S = -1/2$ transition (three additional lines are hidden under the stronger hyperfine components of the $m_S = -5/2 \leftrightarrow m_S = -3/2$ transition). The shift of the $m_S = -3/2 \leftrightarrow m_S = -1/2$ transition with respect to the stronger $m_S = -5/2 \leftrightarrow m_S = -3/2$ transition is caused by the presence of a small zero-field splitting $D = -457$ MHz [6].

To obtain the ENDOR spectra, the magnetic field was fixed successively to each of the six strong hyperfine lines of the $m_S = -5/2 \leftrightarrow m_S = -3/2$ transition. Subsequently the Mims-type [5] pulsed ENDOR technique was used by applying an RF pulse with a duration of 5 μs in the second time interval of the stimulated echo pulse sequence. The frequency of this RF pulse is slowly varied while repeating the complete pulse sequence. The ENDOR spectrum is observed as a change in the intensity of the stimulated echo when a nuclear transition is excited.

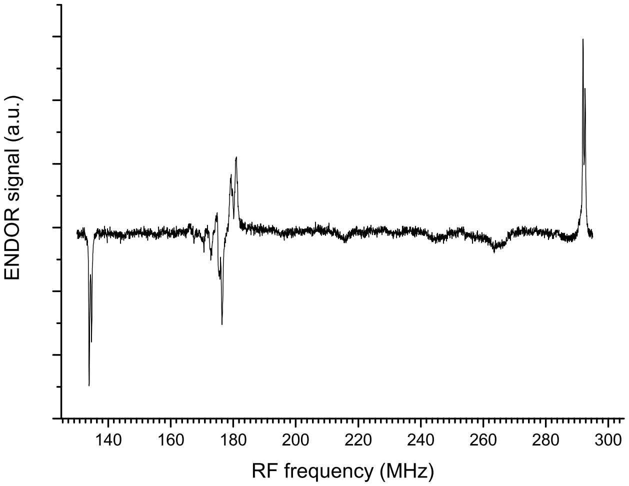

Fig. 3. The ENDOR spectrum taken with the magnetic field perpendicular to the c axis of the $ZnGeP_2$ crystal and fixed at the hyperfine component of the Mn^{2+} ion at $B = 9.8469$ T. The ENDOR signals are obtained by applying a RF pulse between the second and third microwave pulse of a stimulated echo sequence. The change in intensity of the stimulated echo is detected when varying the frequency of the RF pulse. The spectrum represents the average of two consecutive sweeps. $T = 5$ K.

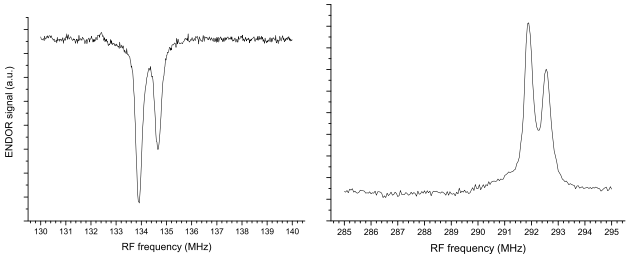

Fig. 4. Detailed recordings of the high-frequency and low-frequency ENDOR transitions of the Mn^{2+} ion in $ZnGeP_2$ as displayed in Fig. 3. The signals are obtained as an average of four sweeps through the ENDOR transitions. The splitting of the lines is caused by the quadrupole splitting of the ^{55}Mn ($I = 5/2$) nuclear spin.

In Fig. 3 the ENDOR spectrum is shown in the $ZnGeP_2{:}Mn^{2+}$ sample with the magnetic field fixed at the center of the intense hyperfine line at 9.8469 T corresponding to the $|m_S = -5/2,\ m_I = 3/2\rangle \leftrightarrow |m_S = -3/2,\ m_I = 3/2\rangle$ transition of the Mn^{2+} ion. This spectrum is taken at $T = 5$ K and obtained by adding two scans, each with a duration of about 20 min. Note the stability of the base line and the size of the RF scan that spans 160 MHz. The set of ENDOR transitions between 170 and 182 MHz is assigned to the ^{31}P ($I = 1/2$) nuclear spin. The lines are displaced from the free ^{31}P nuclear Zeeman frequency of 169.87 MHz in the magnetic field of 9.8469 T by the hyperfine interaction with the electron spin. Since the spectrum mainly serves to illustrate the capability of the 275 GHz spectrometer, we did not perform an orientationally dependent study to assign the various ENDOR transitions to specific *P* sites. We merely mention here that our observation shows that the largest hyperfine interaction with the ^{31}P nuclei has a positive sign and is of the order of 4 MHz. The doublets around 134 and 292 MHz, shown in more detail in Fig. 4, correspond to the two ^{55}Mn nuclear-spin transitions connected to the $|m_S = 5/2,\ m_I = -3/2\rangle$ and the two connected to the $|m_S = -3/2,\ m_I = -3/2\rangle$ levels. From the observed linewidths of 300 kHz, larger than the 50 kHz bandwidth of the RF pulse, we conclude that these ENDOR lines are inhomogeneously broadened. The lines occur at the frequencies $-g_N\beta_N B - (5/2)A + 2P$, $-g_N\beta_N B - (5/2)A + P$ and $-g_N\beta_N B - (3/2)A + 2P$, $-g_N\beta_N B - (3/2)A + P$, respectively, where P is the quadrupole constant of the ^{55}Mn ($I = 5/2$) nuclear spin. From the observed frequencies we conclude that $A = -158.0$ MHz and $P = +0.75$ MHz. The sign of A has been predicted to be negative [6] but to our knowledge this is the first time that this sign has been determined experimentally [7,8]. Our conclusion is based on the possibility to assign the main 6-component EPR line to the transition between the $m_S = -5/2$ and $m_S = -3/2$ magnetic sublevels of the Mn^{2+} ion as a result of the large Boltzmann factor at 275 GHz and 5 K. Similar spectra were obtained when fixing the magnetic field on the other five strong hyperfine lines in the EPR spectrum.

The low-frequency ENDOR lines of the ^{31}P and ^{55}Mn nuclear spins exhibit a decrease of the intensity of the stimulated echo whereas the high-frequency ones show an increase. This kind of phenomenon has been observed earlier and explained as resulting from the interplay between electron-spin, nuclear-spin, and cross-relaxation processes in the regime of large thermal spin polarization [9,10].

To compare the performance of the 275 GHz ENDOR spectrometer with that of our 95 GHz spectrometer [3] we carried out ENDOR experiments at 95 GHz on the same 0.2% Mn^{2+}-doped $ZnGeP_2$ material. At the two frequencies, similar signal-to-noise ratios were achieved but at 275 GHz the amount of material was about 30 times smaller. The ENDOR efficiency, i.e., the fractional change in the EPR signal induced by the RF pulse, was about equal but, owing to the less favourable RF-coil configuration in the 95 GHz set-up, a much longer RF pulse of about 100 μs was required to obtain the optimal ENDOR signal at that frequency. The baseline stability of the ENDOR spectrum at 275 GHz turns out to be much better at 95 GHz owing to the absence of phase-sensitive detection at the output of the intermediate frequency channel.

The second sample is an amorphous, polythiophene-based organic semiconductor. The EPR spectrum presented in Fig. 5, taken at 15 K, is related to the unpaired spin of the holes present in this material. At this low temperature the holes are not mobile but are frozen out on acceptor sites. The spectrum shows the characteristic aspect of a random sample with a *g*-anisotropy. The magnetic field was set at the maximum intensity of this EPR line at 9.8406 T and a stimulated echo was generated at 30 K. When applying a 9 μs RF pulse and scanning the RF frequency, an ENDOR spectrum of the ^{1}H nuclear spins around their Zeeman frequency of 419 MHz could be obtained as a variation of the intensity of the stimulated echo as shown in Fig. 6. The maximum of the ENDOR signal corresponds to a 50% change of the amplitude of the electron-spin-echo signal. At 95 GHz the same type of experiment yields a change of only 5%. The ENDOR linewidth can be understood by assuming a relatively small hyperfine interaction with many ^{1}H nuclei resulting from a wave function of the hole that is distributed over many polythiophene units.

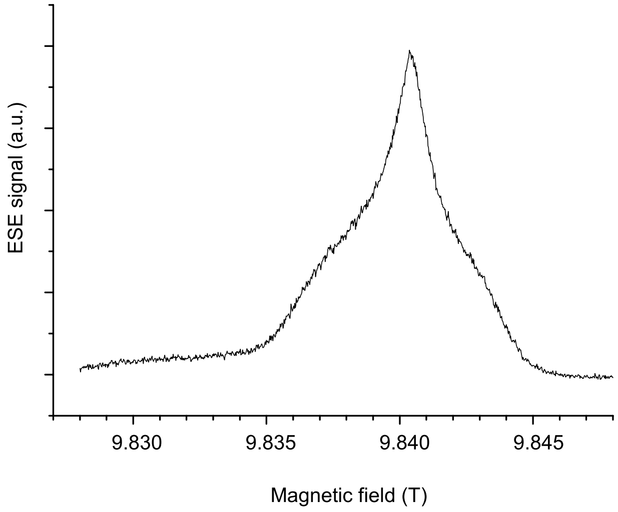

Fig. 5. The stimulated-echo-detected EPR spectrum of an amorphous, polythiophene-based organic semiconductor at 15 K. The three microwave pulses have a length of 250 ns. The first and second pulse are separated by 1 μs and the second and third pulse by 10 μs.

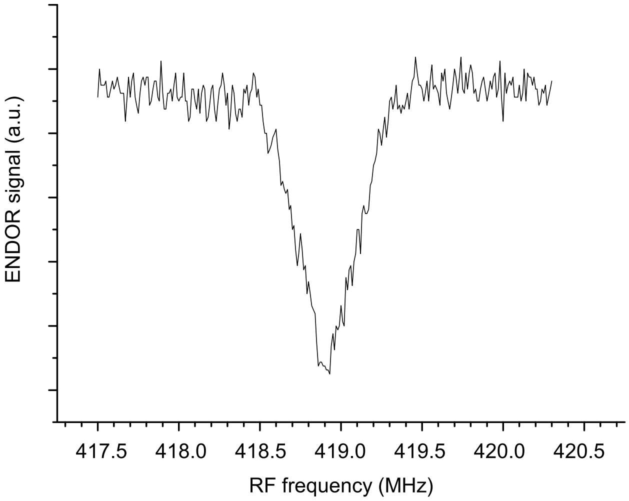

Fig. 6. The ENDOR spectrum of the ^{1}H nuclear spins detected in the EPR signal of the polythiophene-based organic semiconductor displayed in Fig. 5. The ENDOR signal is observed as a change in the intensity of the stimulated echo upon the application of a 9 μs RF pulse between the second and third microwave pulse in the stimulated echo sequence. The microwave pulse duration and intervals are the same as in Fig. 5. $T = 30$ K.

The amplitude of the RF B_2 field can be estimated from the pulse duration needed to saturate the ENDOR transition of the ^{1}H nuclear spins in the case of the polythiophene sample. Although we did not observe nutation effects in the ENDOR signal, our observation that pulses of 20 μs suffice to saturate the ENDOR transition allows us to estimate that an RF field $B_2 \approx 1$ mT is attained in our set-up. This is about what one would expect in view of the input power of 100 W, the dimensions of the ENDOR coil and the position of the sample.

4. Conclusion

The experimental results presented in the previous section show that pulsed ENDOR spectroscopy can now be performed routinely at a microwave frequency as high as 275 GHz. A high spectral resolution is obtained as a result of the large differences in nuclear Zeeman frequencies of different nuclei. The key to this success is the use of a cylindrical single-mode cavity equipped with slits to allow the RF magnetic field to reach the sample. The loaded quality factor of about 1000 allows the generation of microwave magnetic fields with an amplitude of almost 0.1 mT, sufficient to generate $\pi/2$ pulses of the order of 250 ns used in the stimulated-echo sequence of the ENDOR measurements. In addition, a strong RF B_2 field of about 1 mT is generated owing to the fact that the RF coils are positioned at a distance of only 3 mm from the sample.

Acknowledgments

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