Sensitive electron paramagnetic resonance spectrometer for studying defects in semiconductors

H. E. Altink, T. Gregorkiewicz, and C. A. J. Ammerlaan
Van der Waals-Zeeman Laboratorium, Universiteit van Amsterdam, Valckenierstraat 65-67, NL-1018 XE Amsterdam, The Netherlands

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The construction of a state-of-the-art electron paramagnetic resonance spectrometer for application to the studies of defects in semiconductors is described. The spectrometer is of superheterodyne type with low-frequency modulation of the magnetic field and working in dispersion. The use of a microwave synthesizer and a low-noise GaAs field-effect transistor amplifier results in ultrahigh sensitivity of the spectrometer which is experimentally shown to be 3×10^{8} centers cm^{-3} with the test measurement being performed at 4.2 K for the easily saturable typical shallow donor center phosphorus in silicon. It is shown that this high sensitivity can be attributed to the use of the microwave synthesizer. The sensitivity of the spectrometer is improved by a factor 30 when a microwave synthesizer is used as microwave source instead of a quartz crystal stabilized klystron.

I. INTRODUCTION

Electron paramagnetic resonance (EPR) is one of the more prominent spectroscopic techniques applied in solid-state research. The detection methods of the phenomenon, discovered by Zavoisky in the year 1944, have gradually been improved benefiting greatly from the development of the radio- and microwave-frequency techniques in the late forties and early fifties. As a result, the frequency range used in the EPR experiments shifted from about 50 MHz in first experiments to 9 GHz (X band) and higher. This allowed for significant increases of both sensitivity and resolution.

Although the main activity field of the EPR spectroscopy is in inorganic chemistry the method has also been successfully utilized in solid-state physics, including the study of defects in semiconductors. When applicable, i.e., for paramagnetic centers, it has yielded detailed structural information of microscopic character. It should be noted here that the data obtained by EPR and EPR-based double resonance techniques [electron nuclear double resonance (ENDOR), optical detection of magnetic resonance (ODMR)] are in general not accessible by any other experimental method. The power of magnetic resonance spectroscopy is well illustrated by the fact that a microscopic model of the vacancy in silicon, which constitutes a basic building stone for many more complex defects, was developed fully on its basis. Other examples of successful application of EPR in semiconductors are the studies of transition metals in silicon and III-V compounds, as well as the investigations of the most important defect complexes such as EL2 in GaAs and thermal donors in silicon.

A more important disadvantage of magnetic resonance is its relatively low sensitivity compared to some of the other methods. A better sensitivity can be obtained by optical detection of the magnetic resonance (ODMR), however, this is applicable to optically active paramagnetic centers only. This hampers the potential applications of this powerful technique in the studies of high-purity materials and low-dimensional structures. It is therefore of utmost importance to optimize the parameters of the EPR spectrometer for the particular requirements as posed by the paramagnetic centers in semiconductors. These requirements are generally very different from those for which standard commercial EPR spectrometers are designed.

II. PRELIMINARIES

A. Sensitivity

Commercial EPR spectrometers are designed to meet the requirements of the market where one of the biggest fields of application is in inorganic chemistry. In this case the sensitivity of the spectrometer is not a major problem, because of the nature of the measurement. Often the specimen under investigation has a high concentration of paramagnetic centers and saturation of the EPR signal occurs seldom. In such a case the measurements are performed in the absorption mode and high microwave power levels may be used, thus automatically increasing sensitivity.

For EPR measurements in semiconductors, especially for silicon, sensitivity is much more limited by the spin system under investigation. Typical concentrations of investigated centers are in the range of 10^{10}–10^{15} cm^{-3}. At these low concentrations no spin–spin interaction occurs, and so the main deexcitation path is provided by the spin–lattice relaxation. At the same time, in order to avoid impurity conductivity and also to increase the signal by a higher Boltzmann factor, the investigations are mostly performed with the sample temperature close to the liquid-helium boiling point, in the 1–40-K range. However, at such a low temperature the spin–lattice relaxation time is drastically increased and saturation of the signal occurs at relatively small microwave power levels. Under these conditions measuring the dispersion part of the signal is essential to obtain maximum sensitivity, since in the dispersion mode saturation occurs at much higher microwave powers compared to the absorption.

A very much similar reasoning may be employed for choosing the optimal frequency for magnetic field modulation. One should bear in mind that the requirements are contradictory. To obtain a maximum signal the modulation frequency must be equal to the reciprocal of the spin relaxation time. Since, as was mentioned before, in the liquid-helium temperature range the relaxation time is long, the most appropriate modulation frequencies are in the audio-frequency range. On the other hand, however, the detection noise for such low frequencies is prohibitively high. In order to minimize this type of noise commercial spectrometers designed for nonsaturating materials employ modulation frequencies about three orders of magnitude higher, i.e., ≈ 100 kHz. The noise considerations will be discussed in more detail in Sec. II B. An EPR spectrometer working in the dispersion mode is more complex than one operating in absorption mode. However, using modern technology, the more stringent requirements to the spectrometer can be met without highly complex schemes which often are difficult to use and suffer from long-term instabilities. Long-term instabilities can be prohibitive when the spectrometer is to be used also for ENDOR where stability over days is required.

B. Noise

In general the total noise in an EPR spectrometer originates from three independent sources. These are (a) thermal noise at load and detection noise, (b) noise of microwave source, and (c) cavity noise. In what follows these three contributions will be discussed separately.

1. Thermal noise at load and detection noise

This kind of noise is independent of whether measurements are performed in absorption or dispersion mode. Ignoring for the moment other possible noise sources, the signal-to-noise (S/N) ratio is determined at the point where the microwave power reflected from the cavity is detected. If the later stages of the detection system are properly designed, then the minimal amount of noise is the thermal noise at the microwave bridge. The most simple way of detecting microwaves is by microwave diodes, which rectify the microwave power to a dc voltage. However, microwave diodes exhibit an extreme $1/f$ noise, preventing the detection of small signals. The usual procedure to overcome $1/f$ noise is the use of phase-sensitive detection (lock-in technique). This method is very suitable and for modulation frequencies near, or exceeding, 100 kHz it diminishes the $1/f$ noise of the diode below the level of its thermal white noise. The 100-kHz modulation is indeed used in most commercially available spectrometers. However, for the particular applications of EPR as considered here, the use of low-frequency modulation is essential and the $1/f$ noise has to be eliminated in a different way. An obvious solution is amplification of the signal prior to demodulation to audio frequencies. This can be accomplished by heterodyne detection of the signal, by direct amplification of the microwave power, or by a combination of both methods.

In case of heterodyne detection the microwave power reflected from the cavity is converted to a signal at an intermediate frequency (i.f.), by mixing with local oscillator power. Normally the i.f. is of the order of 10 MHz which is substantially higher than 100 kHz and yet low enough to be easily amplified. For the heterodyne spectrometer the detection contribution to the spectrometer noise can be calculated on the basis of the formula of de Vries:[1]

$$F_{\text{spec}}=F_{\text{source}}+\frac{F_{\text{i.f.}}-1}{G_{\text{int}}}+\frac{F_{\text{diode}}-1}{G_{\text{i.f.}}G_{\text{int}}}, \tag{1}$$

where $F=(S/N)_{\text{out}}/(S/N)_{\text{in}}$, with both signal ($S$) and noise ($N$) in power units. The noise figure normally is given as $\text{NF(dB)}=10\log F$. The parameter F_{spec} is the overall noise figure of the spectrometer and $F_{\text{i.f.}}$ and F_{diode} are the noise figures of the i.f. amplifier and the diode, respectively. F_{source} is the noise generated by the microwave source, which is the subject of the next section. G_{int} is the power attenuation of the signal between cavity and mixer, and $G_{\text{i.f.}}$ is the power amplification of the i.f. amplifier.

With $G_{\text{int}}\approx 1$, Eq. (1) shows that if the amplification $G_{\text{i.f.}}$ exceeds the noise figure of the diode the overall noise figure F_{spec} is determined by F_{source} and $F_{\text{i.f.}}$. Instead of heterodyne detection, the same result can be obtained using direct amplification of the microwave power, which is practicable at present and can be performed with low-noise GaAs field-effect transistor (FET) amplifiers.[2] The best noise figure obtainable with a diode is 6 dB against 3 dB (both at 300 K) for the amplifier, where the extra factor 2 is caused by the fact that also the sum frequency is produced in the mixing process or in case of final detection the rectification of the microwave power. Furthermore, the GaAs-FET amplifier can often be cooled to nitrogen temperature, which further reduces its noise figure to 1 dB and makes the application of a microwave amplifier even more advantageous. At this point one should, however, note that although the detection system hardly adds noise, in the case when the GaAs-FET amplifier is operated at liquid-nitrogen temperature, the thermal noise at the circulator, which stays at room temperature, becomes the limiting factor. With the noise figure of an amplifier of 3 dB and high enough amplification, the noise figure of the spectrometer is also 3 dB ($F_{\text{spec}}=2$), provided that F_{source} can be neglected. In order to achieve sufficient amplification a second-stage amplification might be necessary and this second stage can be either a second GaAs-FET amplifier or heterodyne detection.

2. Noise of microwave source

The noise of the microwave source consists of amplitude as well as phase/frequency fluctuations. The amplitude noise of the generator seldom is a problem since it can be successfully overcome by choosing an appropriate detection method. The application of a reference arm, a critically coupled cavity, and balanced mixers cancels this noise for the largest part. The frequency noise of the generator is far more important and becomes a major problem when the spectrometer is tuned to detect the dispersion part of the signal. In this case the spectrometer is sensitive to frequency shifts of the cavity and consequently will respond also to frequency shifts of the generator. The problem is illustrated by the formula giving the reflected power from the cavity when tuned to dispersion (with sample in resonance):[3]

$$P=P_0\left[Q_1\left(\eta\chi'+\frac{2\Delta\nu}{\nu}\right)\right]^2. \qquad (2)$$

In this expression P_0 is the incident microwave power on the cavity, Q_1 is its loaded Q factor, and η is the filling factor (the fraction of the stored microwave power in the cavity that interacts with the sample). The dispersion part of the magnetic susceptibility is given by χ' which has the same phase as the fractional frequency deviation $\Delta\nu/\nu$, in which ν is the eigenfrequency of the cavity. Without these frequency deviations the minimum detectable signal is determined by the thermal noise as described in Sec. II B1. Therefore the noise generated by random frequency deviations of the generator should be less than the thermal noise component. To make an estimate of the required frequency stability of the generator it is convenient to use $\Delta\nu_{\rm rms}/\nu$ of the generator. Normally $\Delta\nu_{\rm rms}$ is expressed in Hz per $\sqrt{\rm Hz}$ bandwidth and here the short term stability (bandwidth of detection) is needed. This $\Delta\nu_{\rm rms}/\nu$ is substituted in Eq. (2) to obtain an estimate of the noise generated by random frequency fluctuations. But it should be noticed that Eq. (2) is only valid for a steady-state situation, so for a stationary frequency deviation $\Delta\nu$,[3] and not for (very) short-term deviations since, in this case, the role of the Q factor is not taken into account properly. Although the use of Eq. (2) represents a rather crude approximation and a detailed calculation cannot be made, the results obtained with it are reasonable and can be used to obtain limiting values of the absolute noise level. On the other hand, the resulting frequency noise is expected to scale with the short-term stability of the microwave generator and relative noise levels should be predicted to a higher accuracy. The thermal noise power is given by (for first-stage amplifier with NF=3 dB) $2kT\Delta f$, where Δf is the detection bandwidth and the noise generated by frequency deviations should not exceed this value. For a bandwidth of 1 Hz this leads to

$$P_0\left(Q_1\frac{2\Delta\nu}{\nu}\right)^2<8\times10^{-21}\ \text{W}. \qquad (3)$$

Since this kind of noise depends on the microwave power it is not possible to give an absolute frequency stability requirement. However, the experimental values $P_0=200\ \mu$W and $Q_1=5000$ can be given as a typical limit where saturation of the dispersion signal starts to occur. Substitution of these values shows that $\Delta\nu/\nu$ should be less than 10^{-12} (for a bandwidth of 1 Hz).

In the practice of EPR spectrometers two kinds of microwave sources are used: klystrons and Gunn diodes.

The advantage of the Gunn diode is the high microwave power and the low voltage power supplies required. However, the phase noise of these generators is a factor of 10 worse than for reflex klystrons, which makes them less applicable for use as the microwave source in a dispersion spectrometer. In the following part the noise of a reflex klystron will be discussed, with most of the conclusions applicable also to Gunn diodes. Some information about the spectral purity of the klystrons is considered in various papers on this subject[4,5] with typical numbers for $\Delta\nu/\nu$ given as 10^{-8}–10^{-10} (bandwidth 1 Hz). Such a relatively high stability is only accomplished when the klystron is externally stabilized. The stabilization is mostly obtained by locking its frequency on the measuring cavity. Such a method can be applied only for absorption measurements since, in this case, the frequency deviations are corrected. It implies that also the dispersion part of the signal is effectively eliminated. For dispersion measurements the klystron has to be stabilized on an external stable reference oscillator. This can be a quartz crystal and the klystron is then phase locked on a high harmonic of the quartz oscillator. In this case the frequency stability is determined by that of the quartz crystal. Alternatively, a reference cavity can be used to externally stabilize the frequency. The best results can in this case be achieved with a reference cavity whose noise is subtracted from the noise from the measuring cavity, resulting in cancellation of the frequency noise of the generator. In order to achieve that goal the two cavities have to be identical, and more important, have to remain identical during the measurement. Such a condition is very difficult to realize in practice. An improvement can be made when a dual-mode cavity is used, which comprises both the measuring and the reference cavity. The results reported[4] are good, but such a dual-mode cavity is difficult to operate and lacks the accessibility of the cylindrical cavity. Another successful method of eliminating the phase noise in dispersion measurements is the use of a loop-gap resonator.[6] In this case the combination of a low Q factor and high microwave magnetic field at the location of the sample result in an excellent signal-to-noise ratio. However, it should be noted that for the spectroscopy of defects in semiconductors, operation at liquid-helium temperature is essential, which puts a number of constraints on the construction of the microwave cavity and until now, no report has been given of successful application of one of the mentioned alternative cavity designs operating in the low-temperature region.

A modern alternative for the externally stabilized reflex klystron is a microwave synthesizer, in which the microwave power is generated directly from an ultrastable quartz crystal. Reduction of the phase noise of the microwave generator allows for improvement of spectrometer performance and still using the existing, often specialized, cavities. Although these synthesizers are commercially available for some time their application in magnetic resonance has been scarce[7,8] and was never considered for a standard continuous wave spectrometer. The big advantage of this solution is that no external stabilization is required; this makes the spectrometer and its operation much less complicated and, at the same time, the resulting short-term stability is far better ($\Delta\nu/\nu\approx1\times10^{-12}$ for a bandwidth of 1 Hz). In the further sections of this article

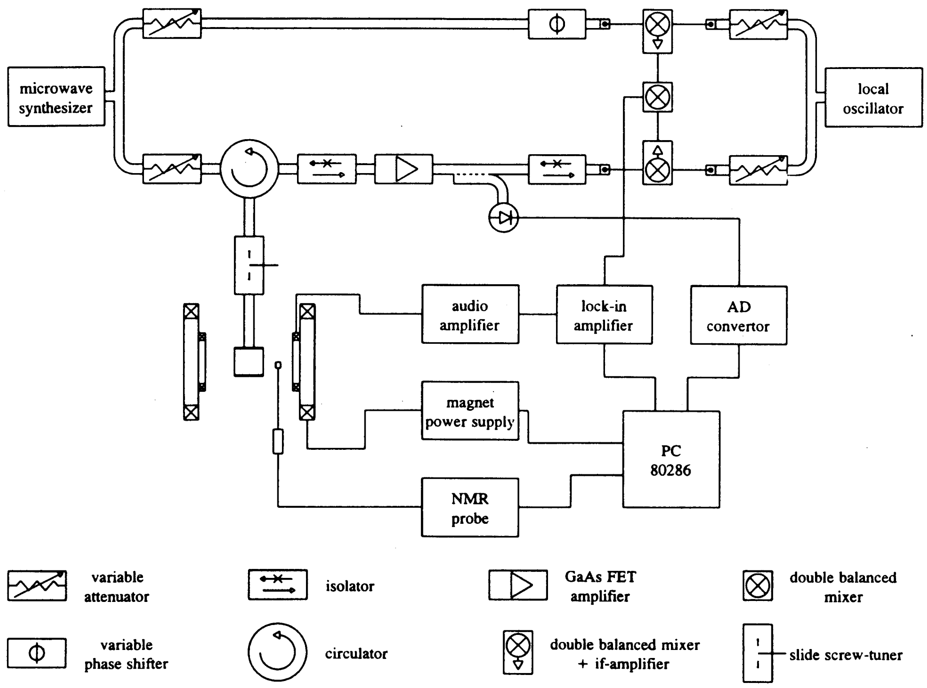

FIG. 1. Block diagram of spectrometer as described in text. All important active and passive components are given. Spectrometer is working in the 8.5–9.5-GHz range (X band).

a direct experimental comparison will be made between the actual performance of an EPR spectrometer as equipped with a klystron stabilized on a quartz crystal and a microwave synthesizer.

3. Cavity noise

The effect of cavity noise is closely related to the frequency noise of the generator, since there is no difference as to whether the source or the cavity has frequency fluctuations. The origin of cavity frequency deviations is believed to be mainly of mechanical nature. These may be due to the imperfections of the cavity, such as the deformations, imperfect contacts between individual parts, and machining tolerances. Also, cooling of the cavity usually introduces strains in the cavity leading to characteristic "cracking" during the experiment. Yet another source of the frequency noise in the cavity is the sample which can mechanically move (vibrate). The same applies also to any kind of (micro) dirt which might be present in the cavity, vibrations in the coupling device, fluctuations in the pressure of the contact gas or vacuum, etc.

For the above-mentioned reasons it is obvious that the noise of cavities of bigger dimensions should be smaller than that of the small ones. This, in part, is responsible for the fact that EPR spectrometers operated at higher frequencies, contrary to expectations, are usually not more sensitive than those tuned for lower frequencies, provided, of course, that detection and frequency noise are minimized.

III. EXPERIMENTAL

A. Description of spectrometer

Following the theoretical considerations outlined in the preceding section an EPR spectrometer was constructed. A schematic drawing of the spectrometer in its final configuration is given in Fig. 1. The spectrometer is operating between 8.5 and 9.5 GHz (X band). A configuration with a reference arm has been chosen to obtain maximum sensitivity,[1] and to permit the spectrometer to be operated always with critically coupled cavity, which is essential when the reflected microwave power is to be amplified. The reference arm also allows for easy tuning to dispersion or absorption by adjusting the phase of the reference microwave power. As discussed before, the detection noise is reduced to a minimum by using a combination of a GaAs FET low-noise amplifier and heterodyne detection at an intermediate frequency of 30 MHz, and therefore this combination has actually been chosen. The GaAs-FET amplifier is from Berkshire Technologies, model x-9.1-30ww, the microwave double-balanced mixers from Triangle Microwave, model PF-80A, and the 30-MHz double-balanced mixer from Hewlett Packard, model 10534A. In first instance a high quality (Varian, type VA 217) reflex klystron stabilized on a quartz crystal was used as a microwave source. As will be shown the sensitivity of the spectrometer in that earlier case was fully limited by the frequency noise of the klystron. Consequently the klystron was replaced by a microwave synthesizer (Hewlett Packard, type 8671A). A comparison of performance of the spectrometer for the two microwave sources will be given. As a local oscillator for the heterodyne detection a reflex klystron, stabilized on the 30-MHz reference signal, is used. In forthcoming improvements it will be replaced by a second microwave synthesizer. Although this will not improve sensitivity, the reliability and ease of operation (no high voltage power supplies and stabilization circuits) will be upgraded. An alternative for a separate local oscillator is the technique described by Hall and Schumacher,[9] where the local oscillator power is derived from the source. But this technique makes operation of a spectrometer more complicated and should only be used in cases where the cost of a generator is prohibitively high (e.g., in higher frequency bands). The microwave bridge is a high performance circulator (isolation ≈ 40 dB), which was preferred over a magic T, since in this latter case half of the power reflected from the cavity is lost in the matched load of this microwave bridge and therefore the sensitivity is reduced by a factor $\sqrt{2}$. The spectrometer is equipped with a (home-built) silver-plated cylindrical cavity operating in the TE_{011} mode. An often used alternative is the rectangular cavity, which has the attractivity of a relatively small size. However, a cylindrical cavity offers several important advantages, the more prominent ones being its high Q factor and the fact that the sample is easily accessible for light or uniaxial pressure. It is also very beneficial that the magnetic field component of the microwaves is always perpendicular to the static magnetic field. This permits an angular dependence of the EPR signal to be taken by rotating the magnetic field instead of rotating the sample, as is the case for a rectangular cavity. A disadvantage of a cylindrical cavity is its size (diameter$\approx$length$\approx$4.4 cm at the X band). In order to fit this cavity between the magnetic pole caps and cool down to liquid-helium temperature a special stainless-steel cryostat, based on thermal conductance, was developed. For an EPR set-up a major advantage of the rigid stainless-steel cryostat over a conventional glass dewar system is its high mechanical stability, which reduces sensitivity to vibrations and ensures stable sample position, even during filling of helium. The magnetic field is modulated at low audio frequencies, generated by a lock-in detector, using external modulation coils. The actual value of static magnetic field, in the range of 0–1 T, is measured to a high accuracy (1 μT) using a proton NMR probe (Bruker, type ER 035M) which is read by a 80286 (AT)PC, which controls the steering current of the magnet. A special algorithm[10] is used to control the magnetic field, also during scanning, within the accuracy of the NMR probe. This is in contrast to commercial spectrometers which actually use Hall probes to measure magnetic field and do not offer active stabilization. It should further be mentioned that the quoted accuracy of the field stabilization applies to short- as well as long-term stability. The latter one is of importance for extension of the spectrometer to ENDOR measurements. The signal is detected using a conventional lock-in detector, the data are sent to a recorder and are read by the PC. Additional digital filtering can be applied to the data; such a procedure is preferred over longer RC times of the lock-in detector.

TABLE I. Specifications of amplifiers and mixers used in spectrometer.

Device	Temperature (K)	Gain (dB)	NF (dB)
GaAs-FET amplifier	300	27	3
GaAs-FET amplifier	77	30	1
Microwave mixer + i.f. amplifier	300	23	8
30-MHz mixer	300	−6	28

B. Noise

In the present spectrometer a combination of a GaAs-FET amplifier and heterodyne detection is used. Specifications of amplifiers and mixers incorporated in the set-up are given in Table I. During construction of the spectrometer in a preliminary phase only the GaAs-FET amplifier was used. Although several high quality microwave diodes were tried, the noise figure of these diodes (at low audio frequencies) was as high as $F=1\times10^4$. This resulted in a final noise figure of the spectrometer $F_{\text{spec}}\approx 20$, which is far from the theoretical goal of $F_{\text{spec}}=2$ as discussed in Sec. II: Preliminaries. Therefore an additional amplification was necessary and here heterodyne detection was preferred over a second GaAs-FET amplifier. The advantage of the heterodyne detection is that for the demodulation of the 30-MHz signal the $1/f$ noise of these diodes is much less, $F\approx 600$, which makes the additional noise of the last mixer fully negligible. This is illustrated by the noise measurements (all with detection bandwidth of 1 Hz and lock-in frequency of 83.3 Hz) of which the results are given in Table II. When the circulator was connected, the spectrometer was tuned to absorption and the incident power on the cavity was very low to ensure that only detection noise was measured. These measurements unambiguously prove that indeed the detection noise is limited to thermal noise of the GaAs-FET amplifier plus the thermal noise at its input. Upon cooling by liquid nitrogen the thermal noise power should be 300/77 times less and taking into account the extra factor 2 in amplification of the GaAs-FET amplifier at 77 K the thermal noise power should be about twice as low. The detected noise voltage should then be lowered by $\approx\sqrt{2}$, which indeed is observed. Furthermore, the total amplification is 50 dB (GaAs-FET amplifier at 300 K), the conversion loss in the last balanced mixer is 6 dB and the total thermal noise at the input of the GaAs-FET amplifier is -171 dBm. This results in a noise power of -127 dBm (2×10^{-16} W) across 50 Ω giving a calculated noise voltage of 0.1 μV. The impedance of the last balanced mixer (50 Ω) and the input impedance of

TABLE II. Measurement of detection noise.

Input GaAs-FET amplifier	Temperature amplifier (K)	Noise (μV)
amplifier off	300	0.02
circulator	300	0.2
50-Ω resistor	300	0.2
50-Ω resistor	77	0.12

TABLE III. Specifications of (stabilized) klystron and synthesizer. The last column gives the theoretical power [based on Eq. (2)] at which the frequency noise equals the thermal noise.

Source	Maximum power (dBm)	Frequency stability		Limit power (dBm)
		Long term	Short term	
klystron	17	5×10^{-8}(/h)	1×10^{-9}(/s)	−78
synthesizer	10	5×10^{-10}(/day)	2×10^{-12}(/s)	−24

lock-in amplifier (10 MΩ) are not matched resulting in the measured value being two times higher than the calculated one.

C. Experimental comparison of externally stabilized klystron and synthesizer

In order to establish the importance of the microwave source stability, the noise level of the spectrometer for both microwave sources was compared. The mentioned combination of GaAs-FET amplifier and heterodyne detection, which gives a minimum of detection noise, was used in both cases. The klystron frequency was stabilized using a commercially available stabilization unit (Microwave Associates, model PLS). The specifications of the (stabilized) klystron and the synthesizer are given in Table III, in which also the theoretical maximum power is given, based on Eq. (2), where the frequency noise exceeds the thermal noise.

The noise measurements were performed at room temperature. A cylindrical cavity with $Q_1=12\,000$ was used. The results are presented in Fig. 2. As can be seen in the case of the klystron at a power of −46 dBm the frequency noise equals the thermal noise and therefore for higher microwave powers no improvement of S/N ratio is obtained. In the case of the microwave synthesizer such a situation is reached only at a power of −16 dBm. This results in an improvement in S/N ratio (in voltage, which is the square root of S/N ratio in power units) of 32. It must be concluded that the estimated required stability by Eq. (2) is too stringent, since comparing the short-term stabilities of the quartz-stabilized klystron and the synthesizer, the expected improvement in S/N ratio should be 500. This is a clear indication that, in the case of the synthesizer, the remaining noise is not caused by frequency fluctuations of the source but by frequency deviations of the cavity. This is in contrast to the case when the klystron is used, the biggest part of the noise, at microwave powers above −46 dBm, is frequency noise of the source itself. This conclusion is further confirmed by the following measurements. At room temperature, with the klystron as microwave source, there was no difference in maximum S/N ratio when the cylindrical cavity ($Q_1=12\,000$) was replaced by a rectangular cavity ($Q_1=3000$). In this case, at higher microwave powers, both the signal and the noise for the cylindrical cavity were four times bigger. This result is to be compared with noise measurements made with the cylindrical cavity at room and liquid-helium temperature. The loaded Q factor at helium temperature is 44 000 compared to the 12 000 at room temperature; therefore it is expected that the noise at helium temperature, at relatively high microwave powers, should be nearly four times higher than the noise at room temperature. Figure 3 gives the noise as a function of the incident microwave power from the synthesizer source at a constant lock-in frequency of 12.3 Hz. Although at helium temperature the noise at higher power levels is slightly bigger, the difference is much smaller (factor 1.5) than the expected value. These measurements confirm the assumption that the remainder of the noise is generated by the cavity.

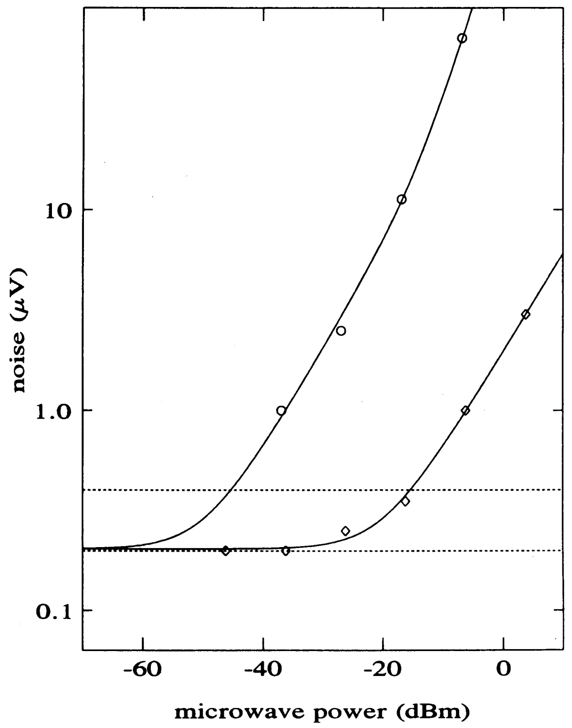

FIG. 2. Comparison of noise of spectrometer in case of klystron (○) and microwave synthesizer (◇). The absolute noise levels are given as a function of microwave power. The lower horizontal line indicates the thermal noise level, the second line indicates the noise level where the cavity/frequency noise equals the thermal noise.

The level of noise was also measured for different lock-in frequencies (cavity at liquid-helium temperature). These results are presented in Fig. 4, which shows that the noise increases with higher lock-in frequencies. This is an argument for the use of low audio frequencies for magnetic field modulation.

From the above described test measurements it is evident that in this particular experimental configuration a microwave synthesizer should be chosen as a source. In this case not only reliability and ease of operation are improved, but also a clear advantage in S/N ratio is obtained. One could also add that, on a long term, a microwave synthesizer proves itself to be a very cost-effective solution.

D. Sensitivity

In order to determine the absolute sensitivity of the spectrometer a sample with a well defined number of spins

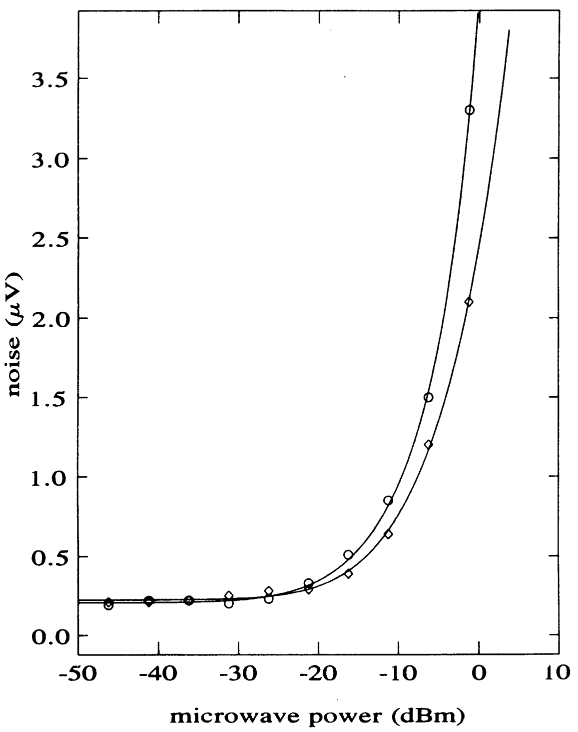

FIG. 3. Comparison of noise at 4.2 K (○) and at room temperature (◇) as a function of microwave power for the microwave synthesizer.

was chosen. The sample was a little piece ($2\times2\times2$ mm^3) of commercially available zone-refined silicon (Wacker) doped with phosphorus. The resistivity of the material was 100 Ω cm which, for uncompensated material, corresponds to a phosphorus concentration of 5×10^{13} cm^{-3}. A phosphorus-doped sample was selected since substitutional phosphorus in silicon is representative for defect centers in semiconductors and as such is typical for the application for which the spectrometer is designed. The measurement was performed at 4.2 K with the spectrometer tuned to dispersion. The modulation frequency was 12.3 Hz and the integration time of the lock-in amplifier was 300 ms. A spectrum obtained for microwave power level corresponding to a maximum *S/N* ratio is given in Fig. 5. The *S/N* ratio as a function of microwave power is given in Fig. 6. The solid line in the figure illustrates the *S/N* ratio without saturation, where the signal at higher power levels is extrapolated from the signal actually measured at low powers. The maximum *S/N* ratio is 55 and 110, with and without saturation, respectively. Using the same data and applying digital filtering (running mean) comparable to a RC time of ≈ 3 s these numbers can be increased to 160 and 320, respectively. Since the sample contains 4×10^{11} phosphorus centers, and the signal is split into two components ($m_I = \pm 1/2$), each line corresponds to 2×10^{11} centers. Since the linewidth is 3 G the minimum number of detectable spins with linewidth of 1 G, when no saturation occurs and with an integration time of 3 s, is therefore 2×10^{8}. For a "normal" sized sample of $2\times2\times30$ mm^3 this gives a minimum concentration of 2×10^{9} cm^{-3}. For a bigger sample of $5\times5\times30$ mm^3, which still easily fits in the cavity without lowering its Q factor, the detectable concentration is 3×10^{8} cm^{-3}.

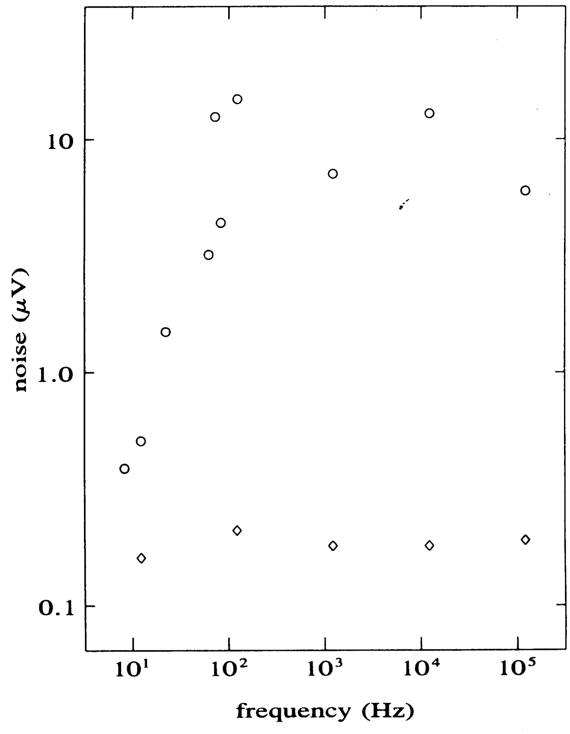

FIG. 4. Noise of spectrometer as a function of detection frequency. Only the detection noise (◇) measured at a very low microwave power (−60 dBm) and total (cavity/frequency) noise (○) at a relative high microwave power (−16 dBm).

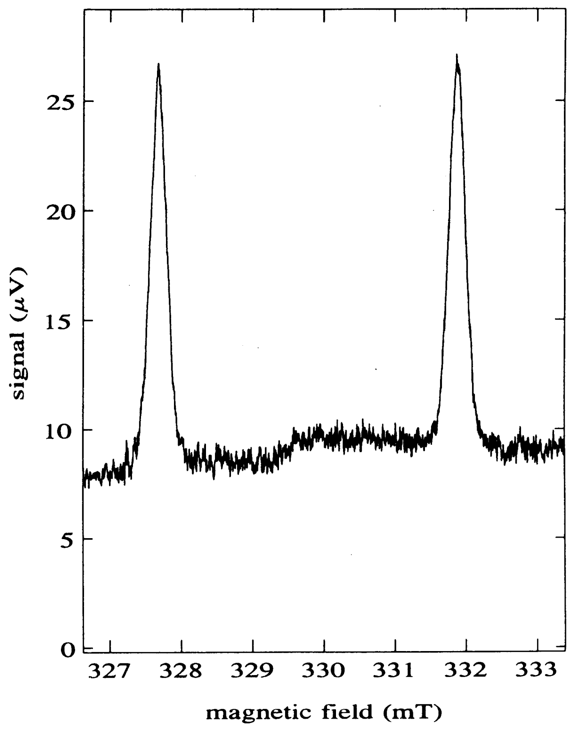

FIG. 5. Example of a spectrum obtained with the spectrometer tuned to dispersion for a Si:P sample. The value for the noise used to determine the *S/N* ratio is its rms value, which equals about one fourth of the width of the noise band. Microwave power is −21 dBm at 9.224 368 GHz. A relatively small offset signal can be seen, which almost always is present in dispersion measurements.

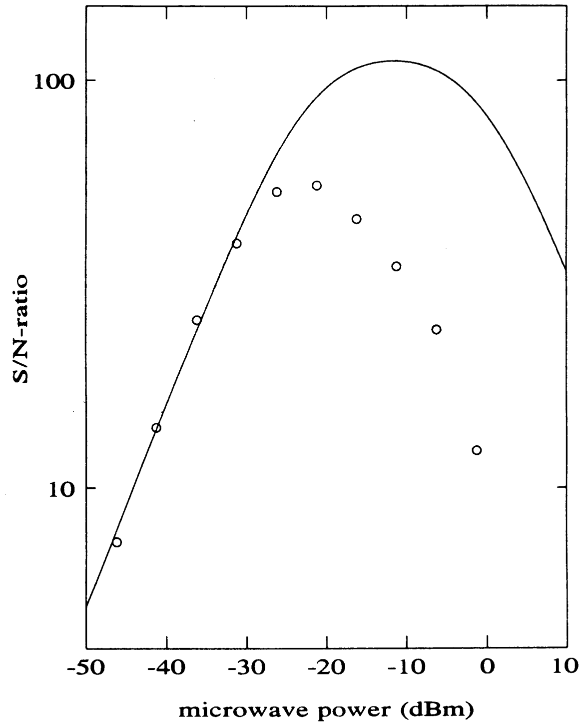

FIG. 6. S/N ratio obtained with the phosphorus-doped silicon sample as a function of the microwave power. The points (○) are the measured S/N ratios and the drawn line is the S/N ratio in the absence of saturation.

When extrapolated to room temperature such sensitivity appears comparable to the highest ones as reported for X-band spectrometers equipped with a loop-gap resonator.[11] For the particular application to the low-temperature studies of defects in semiconductors the sensitivity obtained here is about 50 times higher than the last published one of 10^{10} spins/G^5 and therefore presents a very considerable improvement.

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[1] C. P. Poole, Jr., *Electron Spin Resonance, A Comprehensive Treatise on Experimental Techniques* (Interscience, New York, 1967).

[2] Ch. Hoentzsch, J. R. Niklas, and J. M. Spaeth, Rev. Sci. Instrum. **49**, 1100 (1978).

[3] J. Talpe, *Theory of Experiments in Paramagnetic Resonance,* 1st ed. (Pergamon, Oxford, 1971).

[4] D. T. Teaney, M. P. Klein, and A. M. Portis, Rev. Sci. Instrum. **32**, 721 (1961).

[5] K. L. Brower, Rev. Sci. Instrum. **48**, 135 (1977).

[6] J. S. Hyde, W. Froncisz, and A. Kusumi, Rev. Sci. Instrum. **53**, 1934 (1982).

[7] K. A. Rubinson, Rev. Sci. Instrum. **60**, 392 (1989).

[8] B. E. Sturgeon, and R. D. Britt, Rev. Sci. Instrum. **63**, 2187 (1992).

[9] J. L. Hall and R. T. Schumacher, Phys. Rev. **127**, 1892 (1962).

[10] M. Sprenger, Ph. D. thesis, University of Amsterdam, 1986.

[11] J. S. Hyde, M. E. Newton, R. A. Strangeway, T. G. Camenisch, and W. Froncisz, Rev. Sci. Instrum. **62**, 2969 (1991).