A HIGH PERFORMANCE MM-WAVE ELECTRON SPIN RESONANCE SPECTROMETER

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Abstract - We describe a novel millimetre-wave electron spin resonance (ESR) spectrometer designed to operate in the frequency range 90-200GHz and in the temperature range 1.5K - 270K. The spectrometer uses a bimodal reflection cavity coupled to a circular corrugated guide and uses Gaussian quasi-optics are used for most of the front-end signal processing. This technique has very low insertion loss and allows a number of sophisticated measurement techniques to be employed including induction operation and illumination by both circular polarisation states.

1.0 Introduction

Electron Spin Resonance (ESR) or Electron Paramagnetic Resonance (EPR) describes the resonant absorption of microwave radiation by paramagnetic ions or molecules in a static magnetic field. ESR spectrometers have been a standard tool in biological and chemical diagnostics for many years where it is an established and relatively mature technology. Historically, systems have nearly always operated at frequencies around 10GHz and field strengths around 0.4T. However, recently there has been a growing interest in operation at much higher frequencies in the millimetre-wave range [1, 2, 3, 4, 5].

The main motivation behind this trend has been the greater spectral resolution and the greater sensitivity that may be obtained. Theoretically, the sensitivity increases dramatically with frequency, as $f^{9/2}$, for samples of limited size [6], mainly as a result of the increased filling factor η due to smaller resonators. In practice the increase in sensitivity has been difficult to obtain experimentally, due to a number of factors. This is partly due to the increased dielectric and magnetic losses for many samples at higher frequencies, and partly due to the increased complexity and losses of the experimental apparatus. Operation at 100GHz requires correspondingly large magnetic fields (4 Tesla)which entails the use of a super conducting magnet system operating at liquid helium temperatures in large cryostats.

The most common approach to ESR at high frequencies has simply been to scale 10GHz systems [2], often with the inclusion of an open Fabry-Perot type cavity and oversized waveguides [4] or lenses [5] to reduce losses. We describe a flexible system which uses, quasi-optics to provide a very low loss, highly sensitive spectrometer which still manages to incorporate a number of sophisticated techniques that have been used in lower frequency systems.

These include variable temperature operation from 1.5K to 270K, illumination by circular polarisation states, and induction operation, first described by Portis et al. [7]. Induction operation reduces the effect of spurious reflections, and reduces the effect of frequency and amplitude noise from the source.

2.0 ESR Spectrometer Design

The main features of a continuous wave reflection ESR spectrometer with reference arm bridge are illustrated in Figure 1. The main superficial difference between a mm-wave system and one operating at 10GHz is that a superconducting magnet is required in a large cryostat and the B-field is now parallel to the direction of propagation of the rf field. An ESR spectrum is usually obtained by slowly sweeping the magnetic field while keeping the microwave or mm-wave frequency fixed. The reflected signal from the sample resonator is usually encoded by simultaneously modulating the magnetic field and using a lock-in amplifier after detection. Signals due to dispersion and signals due to absorption may be differentiated by using a homodyne reference bridge.

In standard CW or pulsed ESR experiments, single-mode waveguide is usually used to transmit a linear polarisation state to a resonant cavity. The cavity is usually a rectangular cavity operating in the TE_{012} mode or a cylindrical cavity operating in the TM_{110} mode or TE_{011} mode. Coupling is usually made through a small hole positioned to excite the desired mode in the cavity. In either case, a linear polarisation state is used to interrogate the sample, although it is a single circular polarisation state that is absorbed strongly on resonance. Thus half the power in the other circular polarisation state is effectively wasted, and knowledge is lost of which circular polarisation state is being absorbed.

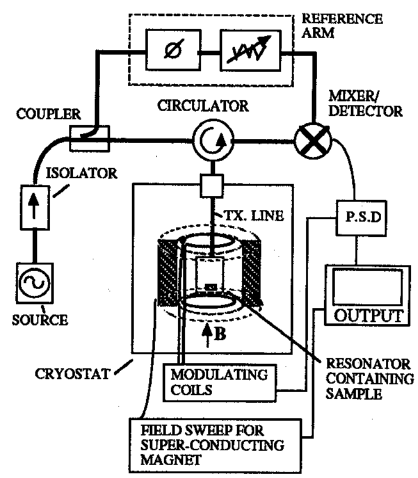

Figure 1. Schematic diagram illustrating the main features of a continuous wave reflection Electron Spin Resonance spectrometer adapted for mm-wave frequencies.

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3.0 New Quasi-Optical System Design

The main design considerations at mm-wave frequencies are concerned with reducing losses and improving the performance of all the components shown in Figure 1.

A number of quasi-optical configurations have been used and Figure 2 shows one illustrative implementation. As illustrated, the system operates in a similar way to the normal ESR system illustrated in Figure 1 but with a number of new and novel features including:

3.1 Quasi-optics - The front end of the system has been constructed using a 'half-cube' optical breadboard [8], which allows great flexibility in the measurement set-up. The half-cubes have a side-length of 120mm and aperture diameters of 88mm. High density polyethylene (HDPE) aspherical lenses are presently used to couple the radiation through the system, and to provide spatial matching to the corrugated waveguide (although these may be replaced by off-axis mirrors). These lenses had quarter wavelength blazing to provide low reflection losses in the 90 GHz region. The rf signal is transmitted as a gaussian beam using scalar corrugated feedhorns. Most of the signal processing is achieved using wire grid polarisers, roof mirrors and free-space, large area Faraday rotators [9,10]. These rotators do not require an external magnetic field and when used as isolators or circulators have given isolations > 50dB with only 0.3dB insertion loss at W-band. A form of Martin-Puplett interferometer is used to create a homodyne bridge to allow changes in absorption and dispersion to be distinguished. This system is analogous to a quasi-optical phase noise measurement system already described [11].

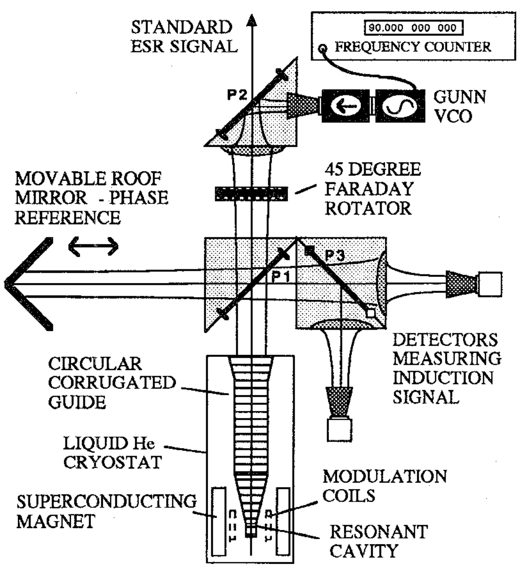

Figure 2. Schematic diagram illustrating the main features of the quasi-optical reflection induction ESR spectrometer. After passing through the Faraday rotator, polariser P1 splits the signal between the resonant cavity arm and the phase reference arm. Any cross-polar signal induced by ESR in the cavity is reflected by polariser P1 towards the detectors. The roof mirror may be used to adjust the phase of the reference signal to allow measurement of absorption or dispersion. P1 and P2 are horizontal (or vertical polarisers). P3 is a 45 degree polariser.

3.2 Transmission Line through cryostat - One of the major design issues at high frequencies is the thermal loading and the insertion loss of the transmission line through the cryostat. We have implemented this transmission line using a thin walled circular corrugated waveguide chosen because of a) the high coupling efficiency between the fundamental free space Gaussian mode and the HE_{11} mode, b) the extremely low propagation loss, of the HE_{11} mode, c) the low coupling to other modes and d) because both linear and circular orthogonal polarisation states may propagate.

This pipe is well over 1.3m long and has a diameter of 27mm and a wall thickness of 300 microns. It is machined from german silver, chosen for its low thermal conductivity and easy machining. (Although stainless steel would offer better thermal conductivity and may be manufactured in lengths >1m. [12]). Using resonance techniques the loss of a 1.3m section of this pipe was estimated to be less than 0.01dB compared to 4-5 dB for single mode waveguide.

3.3 Bimodal Cavity with Mesh/Polariser Coupling - Two cavity configurations that have been successfully implemented are illustrated schematically in Figure 3a and 3b. Figure 3a shows a closed HE_{11} cylindrical corrugated cavity and Figure 3b an open Fabry-Perot type cavity. Two closed cavities have been built. One cavity has the same diameter as the guide (27mm) and the other cavity uses a corrugated horn structure to couple to an electro-formed cavity of diameter 2.8mm. Both horn and cavity are designed to maintain the balanced hybrid mode condition. The open cavity uses a scalar horn structure to produce a 6mm diameter beam waist outside the horn which spatially matches to the cavity mode. In all three cases the cavity walls are thin enough to allow low frequency modulation of the magnetic field, which is produced by two coils situated around the cavity.

Coupling to all three cavities is either via an electroformed square mesh made from copper with >99% reflectivity for both polarisation states or "leaky" tungsten polarisers. These may be easily wound to any desired pitch to give any desired reflectivity for one polarisation state. The polarisers are wound on molybdenum frames to reduce the effect of differential thermal expansion. (The polariser approach is particularly attractive for pulsed induction operation where a low Q system is a requisite).

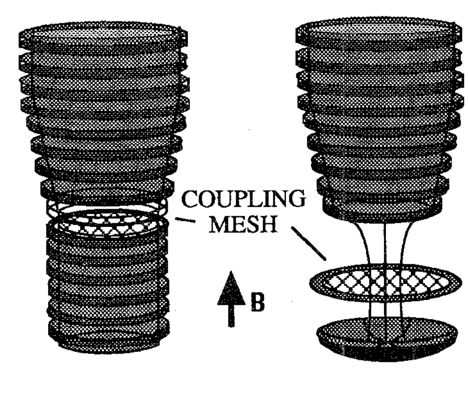

Figure 3 . Schematic diagram illustrating two of the cavity configurations and the coupling to the corrugated guide. a) A closed cavity operating in the HE_{11} transverse mode with mesh coupling and b) An open Fabry-Perot type cavity, operating with mesh coupling, where the cavity mode is spatially matched to the propagating Gaussian mode produced by the tapered horn.

3.4 Cryostat, Magnet and VTI System - The cryostat is a vapour shielded Oxford Instruments design capable of holding 40 litres of liquid Helium. It has a niobium tin superconducting magnet giving 8T (stable to 1 in 10^5 with a high stability power supply). The magnetic field homogeneity is better than 1 in 10^4 over a cylinder 6mm diameter and 20mm high. The cryostat is fitted with an Oxford Instruments Variable Temperature Insert (VTI) with a 49mm diameter bore and an Intelligent Temperature Controller which allows the temperature to be varied from 1.5K to 270K with milli-kelvin stability below 20K. The boil off rate varies depends on the temperature setting but is typically 0.4 litres/hr with an empty VTI and 1 litre/hr with the ESR probe. Thus, it is usually possible to have two days continuous operation before refills.

3.5 MM-wave source - A wideband mechanically tunable Gunn oscillator provides the input signal (initially at 90GHz). This is either stabilised using an EIP counter or locked to the cavity by applying a small frequency modulation to the oscillator and using a phase sensitive detector to provide a feedback signal to the oscillator. We also intend extending the frequency range of the system beyond 180GHz using a frequency doubler.

3.6 Mixer Systems - At present we are using Schottky mixers and detectors at 90GHz, although we also intend using liquid helium cooled InSb mixers at 90GHz and at higher frequencies. These offer wide rf bandwidth and low 1/f noise. Even for a wideband system the noise temperature is 4000K for an i.f. of 100Hz and considerably lower at 1.5K [13]. Low 1/f noise is an important consideration in any homodyne system where the encoding modulation frequency may be low.

4.0 System Configurations

Because the transmission line and cavity supports two degenerate modes with orthogonal polarisations (linear or circular) a number of different useful system configurations may be implemented.

4.1 Standard ESR - A standard ESR signal may be obtained in the conventional manner by illuminating with a single linear polarisation. A free-space Faraday rotator is used as a circulator to direct the co-polar reflected beam to a mixer/detector system as indicated in Figure 2.

4.2 Induction ESR - As well as detecting the co-polar signal it is also possible to detect the cross-polar signal as also indicated in Figure 2. Differential absorption or dispersion (due to ESR) of one circular polarisation state with respect to the other, will cause a signal to be transferred to the orthogonal linear field. If a mesh is used the cross-polar signal will have a similar field strength to conventional ESR. It is stripped off using a wire grid polariser in the quasi-optics above the cryostat and detected using an appropriate mixer system. In both induction ESR and standard ESR a homodyne bridge may be used to differentiate between dispersion and absorption, in the conventional manner.

Induction operation has the advantage that the system becomes much less sensitive to frequency and amplitude noise on the oscillator and there is a large intrinsic rejection of spurious signals caused by unwanted reflections. This allows higher rf powers to be used without spurious reflections saturating the mixer [6,7]. In an ideal system a signal will only be measured if there is differential absorption or dispersion due to ESR. Thus, an important design parameter is the very low cross-polar coupling between the orthogonal linear polarisation states away from resonance. Up to 50dB isolation between the modes has been achieved in practice.

4.3 ESR using circular polarisation - It is also possible to illuminate the cavity using circular polarisation as illustrated in Figure 4. A Martin-Puplett polarising interferometer is used to create either left or right circular polarisation. The reflected signal after passing back through the interferometer has its polarisation flipped through 90 degrees and is directed towards the detector system. Like induction ESR this system has the advantage that no circulator is required. The use of circular polarisation allows the sign of the g factor to be established [6] and increases the useful incident power by a factor of 2.

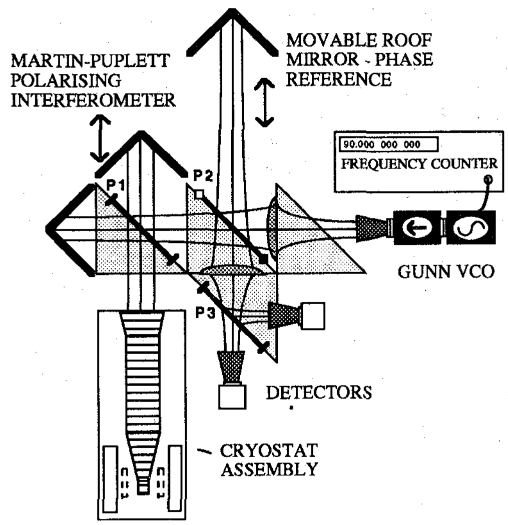

Figure 4 . Schematic diagram illustrating the main features of a quasi-optical reflection ESR spectrometer using circular polarised light. A circular polarised beam is created using a Martin-Puplett Interferometer. Any reflected signal from the cavity will pass back through the interferometer and have its polarisation flipped by 90 degrees and be reflected by polariser P2. A roof mirror may be used to adjust the phase of a reference signal to allow measurement of absorption or dispersion. P1 and P3 are horizontal (or vertical polarisers). P2 is a 45 degree polariser.

5.0 Performance

The spectrometer has been tested successfully at 90GHz in both the standard and inductive ESR mode using small samples of diphenylpicrylhydrazyl (DPPH) using the type of cavities illustrated in Figures 3a and3b. For a cavity length ~6.6mm (4 half-wavelengths) the unloaded cavity Q was ~ 4000 for the open cavity and ~2000 for the large diameter closed cavity at room temperature. The loss from the cavity to the detectors was < 1dB.

A 200μg sample of DPPH showed a 3% change in Q at 210K for a resonance frequency of 90GHz which is also sufficient to cause distortion of the spectrum as indicated by Goldberg and Crowe [14]. This is consistent with theoretical predictions and leaves hope that the sensitivity may be increased by reducing the transverse dimensions of both cavities to improve the filling factor. This change in Q can also be compared to theoretical predictions of Goldberg and Crowe [14] that a 1% change in Q at 9.5GHz would be caused by 250μg of DPPH in a TE_{102} cavity or 100μg in a TE_{011} cavity (for an ideal system operating at room temperature).

At 210K we measured the linewidth of DPPH to be ~ 6 gauss at 90GHz, increasing at lower temperatures to > 70 gauss at 4K. The sensitivity showed the expected 1/T dependence in the 210K to 2.5K temperature range with no sign of saturation.

At present, system noise is dominated by vibrations caused by the very strong Lorentz forces on the modulation coils. These coils are now being repositioned so that there is no direct mechanical contact between the coils and the cavity. Depending on the choice of mixer or measurement, either AM noise on the local oscillator or detector noise is expected to be the limiting noise source.

6.0 Results

As one example of the use of a bi-modal reflection cavity operating at 92GHz, the measured spectrum of a small powder sample of SrM hexaferrite is shown in Figures 5 and 6. This material is of interest because it is the ferrite used in the free space Faraday rotators [9,10]. It is characterised by a very strong uniaxial anisotropy field and a zero field resonance around 50GHz.

This powder sample had a random orientation and was expected to give broad peaks at the two Larmor resonance frequencies corresponding to the two cases of the magnetic field parallel and perpendicular to the anisotropy easy axis [15].

$$\omega = \gamma (H_0 + H_A) \quad \text{and} \quad \omega = \gamma (H_0(H_0 - H_A))^{1/2}$$

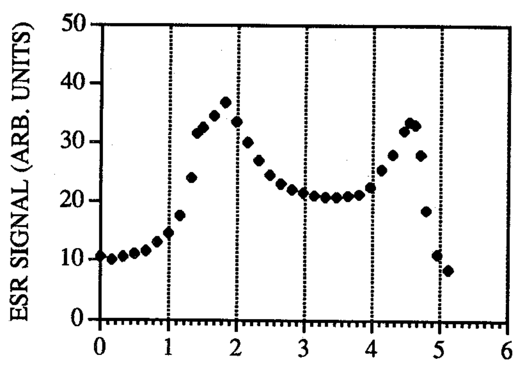

Figure 5. Measured spectrum of a powder sample of SrM hexaferrite at 221K using standard ESR at 92GHz. This was measured simultaneously as the spectrum shown in Figure 6.

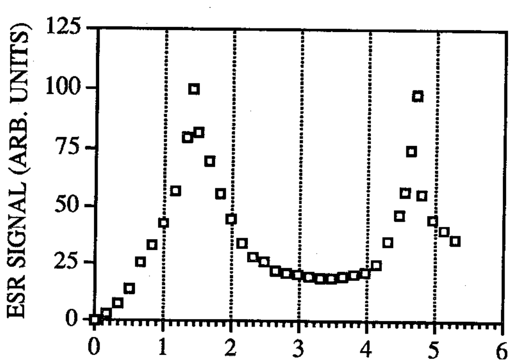

Figure 6. Measured spectrum of a powder sample of SrM hexaferrite at 221K, using inductive ESR at 92GHz. This was measured simultaneously as the spectrum shown in Figure 5.

where H_0 is the applied field and $H_A = 2K_1/M_S$ is the anisotropy field (and where the demagnetisation field has been omitted for clarity). Because of the huge linewidths the spectrum was measured directly and the source was locked to the cavity. Figure 5 is the spectrum given by standard ESR and indicates the total loss as a function of magnetic field. Figure 6 is the spectrum given by inductive ESR and indicates the signal that is caused by differential absorption or dispersion between the two circular polarisation states. It is interesting to note that the spectra shown in Figure 5 and Figure 6 would seem to indicate different resonance frequencies.

It should be noted that ESR below 50GHz would be unable to pick up the parallel resonance, and that conventional ESR could possibly have misinterpreted the spectrum.

7.0 Conclusions

The use of Gaussian beams and quasi-optics for the rf signal processing and the use of the HE_{11} mode corrugated circular pipe in the cryostat offers a very flexible, low loss transmission system for high frequency spectrometers. The use of a bimodal reflection cavity and polarisation discrimination allows much higher rf powers without spurious reflections and frequency noise becoming problematic. This type of system also permits the use of a variable temperature insert which allows the temperature to be varied from 1.5K to 270K.

This is a flexible high performance system that is easily scaled to any desired frequency in the millimetre or sub-millimetre wave range.

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References

1) S.S.Eaton, G.R.Eaton, "Applications of High Magnetic Fields in EPR Spectroscopy", Magnetic Resonance Review, 1993, Vol.16, pp.157-181
2) Y.S.Lebedev, "High-Frequency Continuous-wave Electron Spin Resonance", *Modern Pulsed and Continuous-Wave Electron spin Resonance*, Editors L.Kevan, M.K.Bowman, John Wiley & Sons, 1990
3) E.Haindl, K.Mobius, and H.Oloff, Z.Naturforsch. Vol. 40a, pp.169, 1985
4) O.Burghaus, M. Rohrer, T. Gotzinger, M.Plato, K.Mobius,"A novel high-field/high-frequency EPR and ENDOR spectrometer operating at 3mm wavelength", Meas.Sci.Technol. 3, pp.765-774, 1992
5) W.B.Lynch, K.A.Earle, J.H.Freed, "1mm wave ESR spectrometer", Rev.Sci. Instrum. Vol. 59, pp.1345, 1988
6) C.P.Poole, *Electron Spin Resonance* , Wiley (Interscience), New York, 1981
7) A.M.Portis, D.Teaney, "Microwave Faraday Rotation: Design and Analysis of a Bimodal cavity", Journal of Applied Physics, Vol.29, No.12, Dec. 1958
8) J.C.G.Lesurf, "Millimetre-Wave Optics, Devices and Systems" IOP Publishing Ltd. Adam Hilger 1990
9) G.M.Smith, C.P.Unsworth, M.R.Webb, J.C.G.Lesurf, "Design, Analysis and Application of High Performance Permanently Magnetised, Quasi-Optical, Faraday Rotators", IEEE, MTT Symposium Digest, San Diego, 1994
10) G.M.Smith, C.P.Unsworth, S.Kang, E.Puplett, D.Franklin, J.C.G.Lesurf, "Microwave, Millimeter Wave and Sub-millimeter Wave Free-Space Faraday Rotators", IEEE, MTT Symp. Digest, Orlando,1995
11) G.M.Smith, J.C.G.Lesurf, "A Highly Sensitive Millimetre-wave Quasi-Optical FM Noise Measurement System", IEEE, MTT Vol.39, No.12, pp.2229-2236, December 1991
12) J.Doane, General Atomics, Private Communication
13) K.Wood, QMC Instruments, London, England, Private Communication
14) Z.B.Goldberg, H.R.Crowe, "Effect of Cavity Loading on Analytical Electron Spin Resonance Spectrometry", Analytical Chemistry, Vo.49, No.9, pp. 1353-57, August 1977,
15) M.T.Weiss, P.W.Anderson., "Ferromagnetic Resonance in Ferroxdure", Physical Review, Vol.98, No.4, pp.925-926, 1955