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A New Zero-Field Paramagnetic Resonance Spectrometer*

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The construction of a new zero-field paramagnetic resonance (ZFPMR) spectrometer is discussed. Spectrometer organization and construction details are presented for both resonant cavities and broadband traveling-wave helices as sample holders. A new circuit diagram for a square wave magnetic field modulator with fast rise time is given. The performance of each kind of spectrometer is discussed with particular emphasis on investigation of paramagnetic rare earth ions with zero-field splittings in diamagnetic host lattices.

INTRODUCTION

Zero-field-paramagnetic-resonance (ZFPMR) spectrometry is becoming increasingly important as a method for investigating ground state splittings of energy levels in paramagnetic systems.[1–9] Since no external static magnetic field is applied to the sample, the microwave frequency must be swept until the resonance condition is met. The interpretation of spectra is particularly simple since one may determine energy level splittings directly from the frequency axis, without needing to know the field for resonance at a fixed frequency. In general, the lines are not broadened by inhomogeneity in an applied magnetic field or partially aligned local fields; and, of course, the Zeeman interaction term and second-order Zeeman cross terms are absent from the Hamiltonian. A discussion of some of the uses of ZFPMR has been given by Erickson.[5]

The difficulties associated with the construction of broadband, variable frequency, microwave systems with low or few reflections of power are well known, and therefore magnetic field modulation rather than frequency modulation is usually used. Moreover, since the direction (polarity) of the modulation magnetic field along its axis is not important, the sample acts like a full wave rectifier with respect to the modulation of the energy levels. Hence feeble sine wave modulation is not used to obtain derivative spectra, but rather absorption is presented directly because intense zero-based square wave magnetic field modulation is used to alternately chop between the zero-field and low-field energy levels. Because there is a π phase difference between paramagnetic absorption due to the zero-field and low field levels, the phase sensitive detector output for each has opposite polarity and the difference of the two is presented on the chart recorder. By varying the intensity of the square wave modulation field, different sets of low field levels may be investigated as well as the zero-field levels.

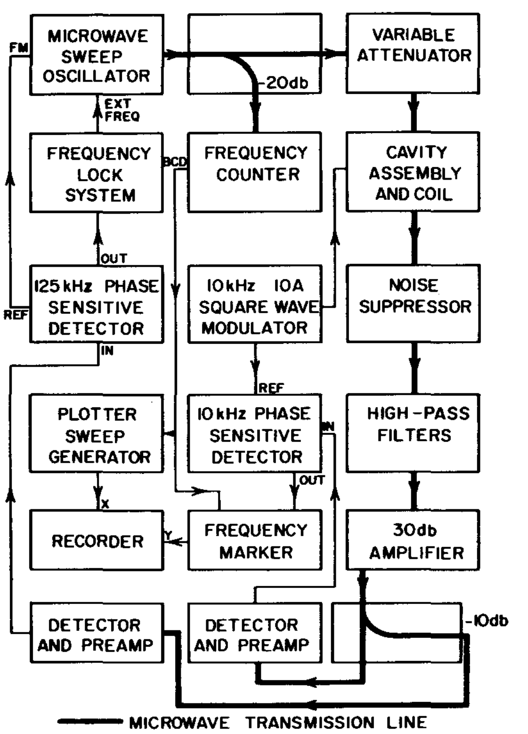

FIG. 1. Block diagram of ZFPMR spectrometer in the cavity configuration. For clarity, the three pairs of Helmholtz coils used to cancel external magnetic fields have been omitted.

There have been a number of experiments[10,11] in the past in which zero-field transitions have been detected because the zero field splitting (ZFS) was known approximately from high field data, and was close to the resonant frequency of a cavity on hand. The static magnetic field from the electromagnet of the high field spectrometer could then be decreased to zero in order to observe the transition.

On the other hand, there have been relatively few attempts to construct a truly broadband spectrometer with which to do ZFPMR as a matter of course. This is necessary because the ZFS may not always be known approximately from high field data. Bleaney, Scovil, and Trenam[1] did a zero-field experiment by dielectrically tuning a number of cavities over a fairly wide frequency range. Later both Mock[2] and Bogle, Symmons and co-workers[3] used a "low Q" spectrometer constructed by filling a waveguide section with sample in order to investigate a number of systems over a wide frequency range. Erickson[5] used a dielectrically loaded tunable cavity with a trombone line stretcher and amplifier to generate microwaves of appropriate frequency (the microwave analogue of a regenerative oscillator or oscillating detector).[12] Urban and co-workers[9] have adapted their variable frequency EPR spectrometer to operate in zero field by using tunable cavities and reflection helices.

Our spectrometer can operate with either resonant cavities or transmission helices as sample holders. We report, in turn, construction details for each type of spectrometer as well as for the devices themselves. We then report the construction of an extremely fast risetime square wave magnetic field modulator for use with either type. This is followed by a discussion of the performance of each type of spectrometer with specific examples from investigations of paramagnetic rare earth S-state ions in diamagnetic hosts.

THE CAVITY SPECTROMETER

A block diagram of the zero-field spectrometer in the cavity configuration is shown in Fig. 1. Microwaves are generated in the 1 to 12.4 GHz frequency region with a power of 10 to 100 mW by a Micro-Power 221 sweep oscillator with appropriate backward wave oscillator (BWO) plug-in units (H102DL, H204DL, H408D, and H812D). A sine wave produced by a Princeton Applied Research 120 lock-in amplifier operating in the internal mode then frequency modulates the microwaves at 125 kHz. The microwaves are then passed through a Hewlett-Packard 779D 20 dB directional coupler. The attenuated portion of the power is counted by a Hewlett-Packard 5248M counter with either a 5254B or 5255A frequency converter. The other portion of the microwave power is attenuated with a Hewlett-Packard 354A variable attenuator which is usually set to 40 dB. The power is then critically coupled into and out of a re-entrant microwave resonant cavity using loop antennas, with an insertion loss of 6 dB.[13] The cavity and its sliding short tuner are described below. The cavity acts as a narrow band discriminator with a Q of about 2000; and if the microwave frequency differs from the cavity's resonant frequency, a 125 kHz amplitude modulation is impressed on the carrier. Below the cavity near the sample is a coil producing the modulation magnetic field (1–10 kHz, 0-*ca.* 100 G). In the presence of paramagnetic resonance absorption by the sample, a 10 kHz amplitude modulation will be impressed on the carrier. The microwaves that are transmitted by the cavity pass through a Narda 562 noise suppressor and into the detection system enclosure which serves as a grounded Faraday cage.

Inside the detection box the microwaves first pass through a high-pass filter formed by a pair of coax-to-waveguide adapters and then through a 30 dB gain low noise Watkins-Johnson linear traveling-wave-tube-amplifier (LTWTA), one of models WJ-268, WJ-269, WJ-271, or WJ-276 as appropriate for the frequency band. The power is then divided in two parts by a Narda 3202B-10 10 dB directional coupler.

The first, attenuated portion is detected by an Alpha D5754A Shottky-Barrier diode forward biased at 50 μA, or equivalent. The detector output is then amplified by a Princeton Applied Research 112 preamplifier and processed by the model 120 lock-in amplifier to determine the intensity and phase of 125 kHz amplitude modulation. In order to make corrections to the microwave frequency so as to make it track the resonant frequency of the cavity, the output signal is applied to an operational amplifier integrator, the output of which is applied to the BWO by the sweeper. This servo lock system easily locks the microwave frequency to the cavity frequency as a motor changes the cavity's dimensions, and hence its resonant frequency. When the cavity frequency is not being swept by the motor, the residual frequency modulation of the microwaves caused by the servo loop usually has a depth less than 10 kHz. The frequency (X) axis of a Hewlett-Packard 7000 AMR X–Y recorder is obtained by taking the BCD output from the counter, calculating its difference from a preset frequency, and then converting this difference to an analog voltage by using a digital-to-analog converter. This provides excellent frequency reproducibility and accuracy from scan to scan.

The major portion of the microwave power is detected in the same manner, and the detector output is amplified by an Ithaco 166 preamplifier and analyzed for 10 kHz component intensity by an Ithaco Dynatrac 391 lock-in voltmeter which is referenced externally by the current being sent to the modulation coil near the sample. In some of the experiments a Princeton Applied Research 118 preamplifier and 124 lock-in amplifier were used instead. A description of the modulator is given below. The output of the lock-in amplifier is then applied to the Y axis input of the X–Y recorder after being passed through a unit that operationally adds frequency markers to it if the microwave frequency is a multiple of either 0.01, 0.1, 1, 10, or 100 MHz, in a manner similar to that described in Ref. 14.

In order to assure that the paramagnetic transitions observed are zero-field transitions, the earth's and other static magnetic fields are cancelled to better than 1 mG over the sample volume, by using three pairs of mutually orthogonal solenoids that are approximately in the Helmholtz configuration. Each pair is fed individually by a constant current power supply.

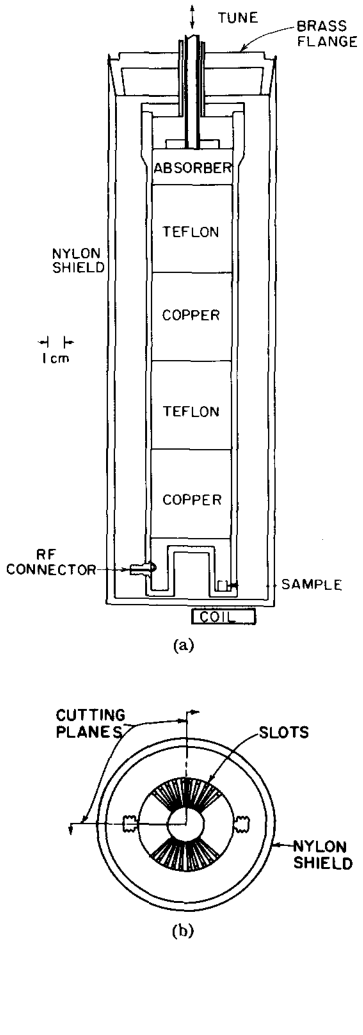

FIG. 2. Schematic diagrams of the tunable cavity assembly. For clarity, the Teflon sheath between the tuner and the cavity wall, rf transmission lines and antenna holders, pumping port, connecting screws, and temperature sensors have been omitted. The entire assembly fits into the tail of a stainless steel liquid helium Dewar. (a) Shows a side view and (b) shows the bottom end view.

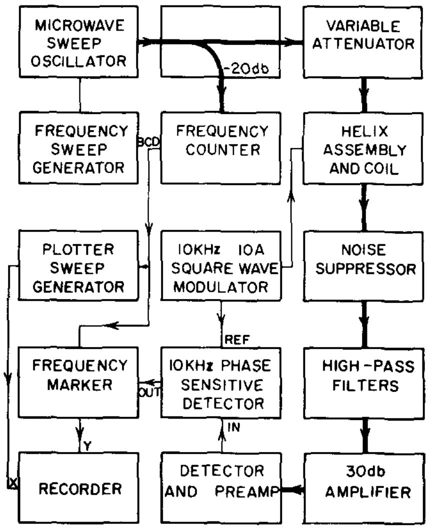

FIG. 3. Block diagram of ZFPMR spectrometer in the helix configuration. Omitted from the diagram are the three pairs of Helmholtz coils used to cancel external magnetic fields —is the microwave transmission line.

THE CAVITY

The cavities we have used are capacity-loaded-coaxial-line resonators as have been described by Moreno.[15] These have been either machined directly or electroformed on a machined Plexiglas mold. The former give slightly better performance, but in both cases the Q of the cavity-sample assembly was an average of about 1500 over the band. All cavities are high purity copper with silver plating. A flash of gold is deposited over the silver to prevent tarnish. This design is small enough to have a reasonably large filling factor and to fit inside a liquid helium Dewar, and yet is broadband enough to allow operation over several gigahertz with high Q. A diagram of the cavity and sample holder assembly is given in Fig. 2.

The antennas are critically coupled, grounded loops. Characteristic impedance is maintained at about 50 Ω through the cavity wall by using Omni-Spectra OSSM 265 bulkhead connectors which have been machined to have circular flanges. A mechanical stop assures the planarity of the connector-cavity wall interface when they are held in their split ring holders. The connector may be rotated about its axis in order to adjust the coupling between the cavity and the transmission line by varying the inclination angle of the loop. This is necessary if samples of different dielectric loss are to be studied.

TABLE I. Physical dimensions and electrical properties of cavities and tuners.

	Cavity I	Cavity II
Cavity—i.d. (cm)	2.782	1.5
Cavity—o.d. (cm)	4.500	4.5
Cavity post—length (cm)	2.470	0.375
Tuner copper spacer—length (cm)	5.000	2.500
Tuner dielectric spacer—length (cm)	5.000	2.500
Tuner—number of copper/dielectric pairs	2	4
Tuner absorber—length (cm)	2.900	5.000
Approx. loaded Q	1500	1500
Frequency range with Teflon disk spacers (GHz)[a]	<1–2.15	2.3–4.6
Frequency range with nylon disk spacers (GHz)[a]	<1–2.25	1.9–4.65
Frequency range with nylon rod spacers (GHz)[a]	<1–1.85	...

[a] This range is to be considered the one in which this cavity-tuner combination is useful for ZFPMR. The cavity and tuner each has its own range, and the frequency range of the combined device is a complicated function of the dielectric constant.

We have chosen to use a quarter-wavelength noncontacting sliding short for tuning the cavity resonant frequency that is similar to the design used by Larson and Hunter[16] for rectangular waveguide. The circular short slides inside a 0.005 cm thick Teflon sleeve, so there is no metal-to-metal contact between the short and the cavity. This tuner consists of alternating disks of copper and dielectric that are each one quarter wavelength long, and are held together by very small nylon screws. The copper pieces are plated like the cavity and are hollow to reduce the heat capacity and mass of the device (see Fig. 2).

The center frequency of the band in which a particular cavity will resonate may be varied by changing the dielectric material in the short. We have varied the effective dielectric constant over a range from about 1 to 4 by using either minimum diameter nylon rods, or Teflon or nylon disks the same diameter as the copper pieces. To prevent microwave leakage at the top of the short, a piece of Emerson and Cumming HF155 high loss dielectric is placed over the top dielectric piece. Placing this absorber in position allows the cavity to work equally well with or without a top cover.

The short moves about 1 cm without rotating to achieve tuning over the entire cavity range. This distance is long enough so that microphonics do not cause much fluctuation of the cavity's resonant frequency. We feel the broadbandedness of this type of tuner is superior to the use of dielectric loading of the cavity interior in order to achieve tuning. Also the wide range of dielectric materials available with low loss tangents allows one to considerably extend the ranges over which a particular cavity will operate. A list of cavity dimensions and frequency ranges for various dielectrics in the tuner that we have used to date may be found in Table I.

The entire cavity assembly is enclosed in a nylon barrier shield which prevents cryogenic fluid from entering the cavity through the radial slots in the bottom. These radial slots allow the modulation magnetic field to enter the cavity by destroying the eddy currents in the cavity wall which would tend to exclude it. The field is generated by a solenoid under the sample and outside the shield. This coil, which is less than 2 cm from the sample, is wound from superconducting wire during liquid helium experiments to prevent excessive Joule heating and vaporization of the helium. The flange onto which the nylon barrier shield fits contains hermetic seals which allow feedthrough of the microwave transmission lines, thermocouples, a mechanical rod for cavity tuning, and a pumping port which allows the cavity to be evacuated during use. Apiezon N grease is used to mount the sample in the cavity near the post and over the slots. The nylon shield is sealed to the brass flange with kerosene based rubber cement.[17]

THE HELIX SPECTROMETER

For many experiments we have used a microwave helix for a sample holder, rather than a resonant cavity. A block diagram of the spectrometer organization with the helix is shown in Fig. 3. Microwaves are generated, counted, and attenuated as in the cavity spectrometer. Since the helix is a broadband device, there is no need to lock the microwave frequency to it and hence there is no need to frequency modulate the microwaves. The residual frequency modulation is that of the oscillator, less than 1 ppm of the microwave frequency. The microwave frequency is programmed by a resistance programmed voltage rapm applied to the BWO by the sweeper.

A pair of coils for magnetic field modulation surrounds the helix with its axis either parallel or perpendicular to the helix axis. For single crystal work it may be desirable to rotate the crystal in order to change the angle between a crystal axis and the modulation field axis. With the pair axis perpendicular to the helix axis, this can be easily done by rotating the crystal about the helix axis by using a rod to the top of the Dewar. These modulation coils are driven in the same manner as with the cavity spectrometer.

The microwave power transmitted by the helix is detected by the same arrangement as in the cavity spectrometer, except the directional coupler, lock system detector, and its associated circuitry are eliminated. In the presence of a paramagnetic resonance signal, the microwaves are amplitude modulated at the magnetic field modulation frequency and this signal is processed in the same manner as in the cavity spectrometer.

THE HELIX AND COUPLERS

The helices are of the transmission type, rather than the reflection type previously used in ZFPMR experiments.[9] We have also attempted to make the match between the helix and the transmission lines as good as possible by using transformer type couplers similar to those described by Chen.[18] Using this arrangement, we have been able to achieve VSWR's less than two over the frequency band of each helix. The helices were designed with the intent of being broadbanded, rather than having higher effective Q over a narrow band. The effective system Q is high because the helix is a slow-wave structure and in principle gives as high a concentration of the microwave magnetic field as a resonant cavity. A discussion of their use in high field spectrometers may be found in a paper by Wilmshurst.[13] The helix and coupler assembly is shown in Fig. 4.

The dimensions and pitch of the helices and couplers we have used to date are given in Table II. Each helix is wound from tungsten alloy wire, which is hydrogen fired and silver plated after winding. The counterwound helical windings in the couplers are ordinary copper wire. The sheath containing the helix itself is constructed of nylon, and the sheath containing the helical couplers is grooved Teflon. The outer shield of the couplers is copper. The length of the windings in the couplers is adjusted in order to optimize the match between the helix and the transmission line.

The helix is operated in a vertical position. The sample is held in place inside the helix by Teflon screws that are threaded to screw loosely into it. If the sample is to be rotated about the helix axis, it is attached to a quartz rod

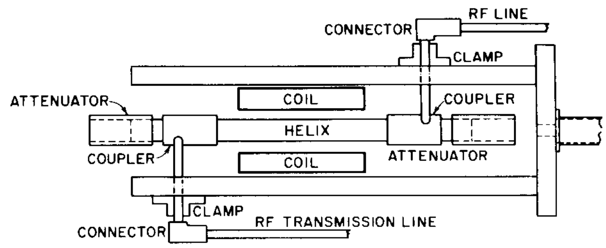

FIG. 4. Schematic diagram of the side view of helix and coupler assembly. The entire assembly fits into a stainless steel liquid helium Dewar so that the center of the helix is level with the axis of the two Dewar windows. This axis is perpendicular to the plane of the page. For clarity some detail has been removed from the rf connectors, coupler clamps, and holder mechanism. Also temperature sensors and other wiring have been omitted.

that fits into the top end. The ends of the helix sheath are coated with Aquadag in order to attenuate microwave power reaching the end of the helix. Additional attenuation is achieved by covering the ends of the helix with a 0.010 cm thick sheath of Teflon embedded with windings of 0.025 mm diam Evanohm nickel–Chromel wire.

THE MODULATOR

The modulator is designed to deliver a rectangular current pulse through either a solenoid or an approximately Helmholtz pair in order to produce a corresponding magnetic field of rectangular intensity. An appropriate voltage spike is added to the leading edge of the driving waveform to increase the rate of rise of current. Such a spike is generated automatically at the trailing edge by the inductive discharge resulting from the interruption of the driving current. The selected coil inductance(s) represents a compromise between conflicting requirements for minimum risetime, maximum current, and maximum magnetic field intensity. In order for the square wave corner to be as sharp as possible, one wants the coil inductance to be as low as possible, without requiring the current to be so large for the field desired that the joule heating of the cryogenic fluid is severe. We have constructed a circuit that will produce a 1 to 10 kHz current square wave with rise and fall times of less than 2 μsec which will deliver currents up to 10 A. At slightly reduced output one may modulate the sample at a rate as high as 40 kHz.

TABLE II. Physical dimensions of helices and couplers.

	Frequency band	
	1–2 GHz	2–4 GHz
Helix tungsten wire—diam (cm)	0.064	0.051
Helix—pitch (tpi)	14	18
Helix—i.d. (cm)	0.737	0.452
Helix—o.d. (cm)	0.864	0.553
Nylon sheath—i.d. (cm)	0.866	0.556
Nylon sheath—o.d. (cm)	1.111	0.655
Coupler copper wire—diam (cm)	0.091	0.091
Coupler helix—pitch (tpi)	9	12
Coupler helix—length (turns)	5.25	2.5
Coupler helix—i.d. (cm)	1.123	0.658
Coupler helix—o.d. (cm)	1.306	0.840
Coupler grooved Teflon sheath—i.d. (cm)	1.189	0.762
Coupler grooved Teflon sheath—o.d. (cm)	1.387	0.919
Coupler copper shield—i.d. (cm)	1.389	0.922
Coupler copper shield—o.d. (cm)	1.588	1.123
Coupler copper shield—length (cm)	2.86	1.725
Attenuator—i.d. (cm)	1.111	0.662
Attenuator helix—pitch (tpi)	7	9

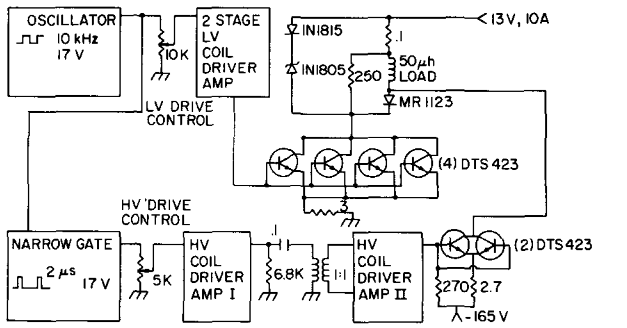

FIG. 5. Block and partial schematic diagram of ZFPMR modulator. All resistances are given in ohms and capacitances in microfarads. Power supplies have not been shown. The entire circuit may be obtained on request.

The solenoid used with the cavity arrangement consists of 40 turns of AWG 16 copper wire on a radius of 1.62 cm. The coil inductance is about 40 μH, and the copper wire is sometimes replaced with superconducting wire. The approximately Helmholtz pair used with the helix spectrometer consists of 20 turns in each coil on a radius of 1.88 cm with a separation of 1.25 cm. The magnetic fields produced at the sample are then about 50 and 80 G, respectively.

A block diagram of the modulator circuits is given in Fig. 5. The principles of operation are roughly as follows. An oscillator generates a 17 V zero-based square wave at the desired modulation frequency. This square wave drives both the low and high voltage sections of the coil driver. These sections are independent except for their coupling at the load coil. The low voltage section operates as follows: The oscillator output is dropped across a 10 kΩ potentiometer which sets the low voltage current through the coil. The current through the wiper is then amplified by two stages of current gain and during the ON part of the cycle turns on four Delco DTS423 transistors which have their collector and emitter leads in parallel. During the OFF part of the cycle, these transistors are reverse biased (−6 V) to assure that there is minimal current flow through the coil.

The high voltage section which produces the voltage spikes is organized as follows. The oscillator output drives a circuit which generates a zero-based 17 V narrow gate of 2 μsec duration for the current risetime. Its output is dropped across a 5 kΩ potentiometer which sets the high voltage level which will be put across the coil at the beginning of the ON part of the cycle. The current from the wiper is then amplified by one stage of current gain and the resultant pulse is transformer coupled to the next stage of current gain. The pulse is then applied to two DTS423 transistors in parallel with 165 V across their common collectors and emitters.

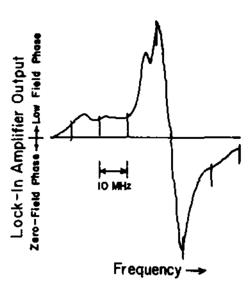

FIG. 6. Typical portion of ZFPMR spectrum of 0.1 mole% Gd^{3+} doped into CaF_2 at 4.2 K using the cavity configuration with Teflon dielectric in tuner. The modulation current was 4 A into an 80 turn superconducting coil. The peak intensity represents a detector signal of about 300 μV at 10 kHz. The frequency markers are spaced by 10 MHz.

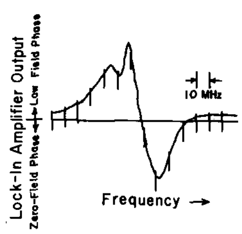

FIG. 7. Typical portion of ZFPMR spectrum of 0.1 mole% Gd^{3+} doped into CaF_2 at 77 K using the helix configuration. The modulation current was 10 A into a pair of coils of 20 turns each with their axes perpendicular to the helix axis. The peak intensity represents a detector signal of about 60 μV at 10 kHz. The frequency markers are spaced by 10 MHz.

The current wave form is monitored by observing the differential voltage drop across a 0.1 Ω noninductive resistor in series with the coil. In order to determine that the magnetic field is zero during the OFF part of the cycle, we have clipped the differential voltage and measured the residual current at high gain. The residual current so measured is less than 2 mA and hence the sample sees less than a 10 or 15 mG field depending on which modulation coil is used, during the zero-field measurement. This measurement is an upper bound since our ability to measure the residual current is limited by the common mode performance of the differential amplifier used.

The magnetic field that is produced contains many odd harmonics of its fundamental frequency, and the high frequencies present have necessitated the elaborate shielding and noise suppression techniques used before detection as described above. If these techniques are not used, pickup problems are severe since they occur at the modulation frequency.

DISCUSSION

Examples of both cavity and helix spectra for an absorption of 0.1 mole% Gd^{3+} doped into CaF_2 are given in Figs. 6 and 7. The sample used with the cavity was a disk 1 cm diam and 0.375 cm high, and the helix sample was a rod 0.4 cm diam and 5 cm long. They contain 7.2×10^{18} and 1.5×10^{19} spins, respectively. Accounting for the difference in sample size, one finds that our cavity is about a factor of 10 more sensitive than the helix for approximately equal modulation currents. The ratio of sample to total interior volume in the case of the cavity was about 0.23 and in the case of the helix was about 0.33 for the above samples of typical size. These spectra were taken with low microwave power and with low amplifier gain. With our existing equipment we can increase the microwave power by a factor of 10^4, which in the absence of saturation should lead to an increase of 10^2 in the resonance signal. Also, we have a factor of 10^5 more amplifier gain available, so with a suitably long time constant, the spectrometer should be able to detect 10^{12} spins, for absorptions of this intensity.

Since our cavities and helices are about equal in the sensitivity they can provide when designed to have broadband frequency characteristics, the decision on which to use must be based on other factors. The mechanism for tuning the cavity and locking the microwave frequency to its resonant frequency is considerably more complicated than that necessary for using the helix. Also the amplitude modulation of the microwaves due to the servo lock system is a source of out of band noise at the detector. On the other hand, it is far simpler to construct new cavities than new helices and couplers, once the cavity tuning mechanism exists. Also, once a particular cavity has been machined, it is simple to extend its range by varying the dielectric material in the sliding short. However, for ENDOR and optically detected or excited state ZFPMR, a helix may be more convenient because of the comparative ease of introducing radio frequency or optical radiation onto the sample. Also, cryogenic fluid may be allowed to flow inside the helix, but not in the cavity, because fluctuations in the dielectric constant due to bubbles do not degrade the performance of a broadband device, but cause random fluctuations in the resonant frequency of a cavity. Also, to insure maximum filling factor for a given sample when using the helix, the distance between the couplers may easily be adjusted.

Detailed discussion of ZFPMR spectra of rare-earth ions, such as those presented here will be forthcoming.

ACKNOWLEDGMENTS

We are grateful to Stanley Schweitzer for design of the frequency-counter-derived recorder sweep generator, A. W. Weissenburger for design of the modulator, and both for many valuable discussions pertaining to various parts of the system.

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†National Science Foundation Trainee, 1969–70.

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