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A Superheterodyne Spectrometer for EPR and ENDOR*

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A superheterodyne spectrometer in X-band for electron-paramagnetic resonance and electron nuclear double resonance is described. The spectrometer employs just one klystron and combines oscillator phase locking and sample cavity locking. The spectrometer sensitivity is 10^{12} *AH* spins.

Descreve-se um espectrômetro super-heterodino em banda X para ressonância paramagnética eletrônica e ressonância dupla eletrônica-nuclear. O espectrômetro usa apenas um klystron e combina amarração em fase a um oscilador e a cavidade da amostra. A sensitividade do espectrômetro é de 10^{12} *AH* spins.

1. Introduction

Many different schemes for microwave spectrometers have been tried and general reviews are found in Poole[1] and Alger[2].

It is generally acknowledged that superheterodyne detection provides higher sensitivity and resolution than homodyne detection, even though it is more complicated, requiring a delicate balancing of the microwave bridge. Feher, in a classical article[3], has discussed the problem of sensitivity in microwave spectrometers and has demonstrated the superior perfor-

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mance of superheterodyne detection at low power levels (less than 10-' w), where the predominating noise is the $1/f$ crystal detector noise. With the use of high modulation frequencies (generally 100 kHz) and improvement in detector crystals, the homodyne detection approaches the superheterodyne and may be superior at high microwave powers.

In a superheterodyne spectrometer it is necessary to operate with the microwave bridge nearly balanced to avoid overloading the IF amplifier. To obtain high sensitivity one employs high-Q cavities. Therefore, slight changes in klystron frequencies modify the power reflected from the cavity creating frequency modulated noise *(FM* noise).

Stabilization of the tlystron is important in eliminating FM noise and achieving long runs without requiring the tuning of klystron frequency to the sample cavity. This is specially important for ENDOR, where the signal is generally weak and very slow sweeps are needed to obtain reasonable spectra. The stabilization of the klystron is achieved by stabilizing the power supply, stabilizing the klystron temperature and locking the klystron frequency tc a reference frequency.

Most spectrometers employ an automatic phase control *(AFC)* to one of the following references: a) sample cavity, b) high Q reference cavity; c) crystal oscillator.

The *AFC* to the sample cavity is extremely convenient because the klystron follows the cavity in its frequency drift. The *AFC* to a reference cavity has the following advzntages: *a)* the spectrometer can be tuned to observe absorption or dispersion; b) the *AFC* is maintained independently of power limitations in the sample cavity; c) the *AFC* is not affected by lossy samples or by the magnetic resonance occurring in the sample.

The *AFC* to a crystal oscillator has the advantages of the previous system, in addition to it allowing a higher frequency stability (a few parts in 10^7) and a simplified frequency measurement.

The spectrometer described in this article, which is a modified version of the apparatus developed by Gazzinelli and Mieher[4], combines crystal oscillator phase locking and sample cavity locking. This is achieved by employing an *AFC* loop to lock the klystron to a crystal oscillator and a second *AFC* loop to lock the *IF* reference standard to the sample cavity. Thus one keeps the high stability characteristic of crystal oscillator locking and the convenience of sample cavity locking.

The spectrometer employs just one klystron, thus gaining in simplicity.

2. Apparatus

Figure 1 shows the block diagram of the EPR-ENDOR spectrometer. It employs one klystron and two locking loops.

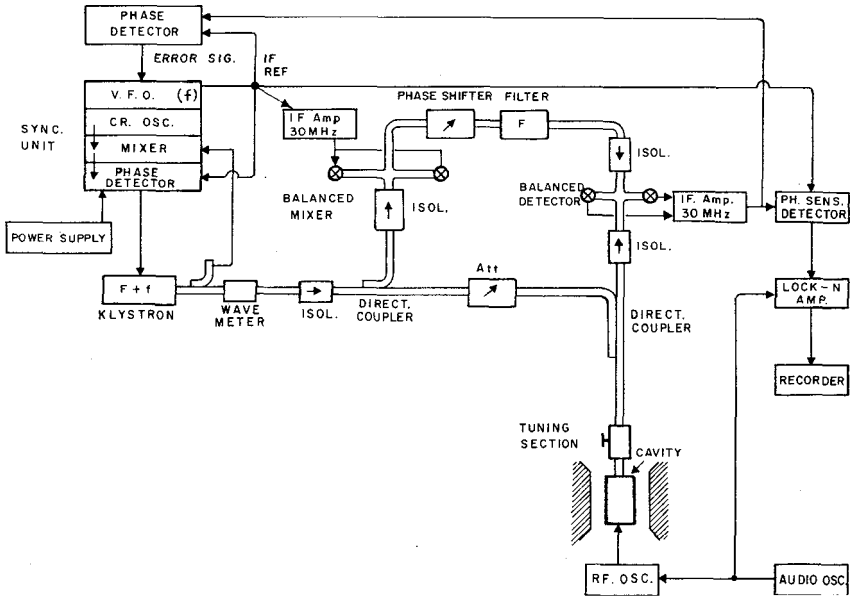

Fig. 1. Schematic diagram of EPR-ENDOR spectrometer

The klystron (VA-242E) is locked to a crystal oscillator by an oscillator synchronizer (Hewlett-Packard, model DY-2650A). A sample of the klystron signal is diverted by a directional coupler (20 db) to this unit and fed to a mixer. This signal is beat against a harmonic of frequency F provided by a 100 MHz temperature stabilized crystal oscillator, and generates a frequency of about 30 MHz. This beat signal is fed to a phase comparator to be compared to a signal generated by a variable frequency oscillator (frequency f : 29 MHz to 31 MHz), which is employed as standard reference frequency for the whole system. The error signal is added to the klystron reflector voltage correcting any drift and maintaining its frequency in the value $F + f$. The short t e m stability is 1 part in 10^8 averaged over 1 second. The frequency of the klystron is manually controlled in the range of 2 MHz, through the VFO control. This allows easy tuning of

the spectrometer and easy frequency measurement: the observation of the VFO calibration allows one to measure the frequency with a precision of 1 part in 10^5.

The power from the klystron is split in two arms. One arm takes the carrier frequency $(F + f)$ to the sample cavity through a wavemeter, attenuator, isolator, directional coupler and tuning section. The signal reflected from the cavity is taken to a balanced detector.

The second arm leads to a balanced mixer magic T, where the carrier frequency is excited by a signal coming from the VFO. The mixer provides three frequencies: F, $F + f$ and $F + 2f$. An interesting feature of this system is that one of the sidebands has the frequency F of the crystal oscillator. This permits tlie use of a narrow band filter (10 MHz bandwidth) to filter out the central frequency and the upper sideband without the inconvenience of power change by detuning. The local oscillator signal is taken to the balanced detector through a phase-shifter and isolator. This phase-shifter is employed to select the correct phase in order to lock the klystron to the sample cavity.

The microwave detector is a balanced mixer magic T employing IN 23F microwave silicon diodes. The power reflected from the cavity is fed to the E arm and the local oscillator power to the H arm. The diodes are matched and the arms of the T are carefully balanced to avoid any local oscillator power escaping to the cavity. The diode currents are measured to allow adjustment of local oscillator power to the optimum value. The intermediate frequency detected is amplified approximately 60 db by a 2 MHz wide band amplifier.

A sample of the signal is taken to a phase sensitive detector where it is compared with the reference signal provided by the VFO. The phase comparator will sense immediately any phase deviation resulting from a drift of the sample cavity and will provide a voltage proportional to the cosine of the phase difference. This error signal is applied to the VFO through varicaps which correct the frequency f, and so the klystron frequency (F + f) remains tuned to the sample cavity. This completes the second locking loop.

The whole system is stabilized in short term in the crystal oscillator and VFO. This will give a stability of about 100 Hz or 1 part in 10^6. However, in long term, the system is locked to the sample cavity following it slowly as it drifts.

The signal from the balanced detector is detected by a 30 MHz phase sensitive detector. A delay line is employed to adjust the standard reference to observe absorption. In principle, one could also observe dispersion, however in this mode the signal is inhibited by the sample cavity locking. The signal is again detected by a lock-in detector tuned to the magnetic field modulation (in EPR) or to the R F modulation (in ENDOR) and recorded.

To induce nuclear transitions it is necessary to feed an R F signal to the sample. Different arrangements are employed in practice; in this spectrometer we used a scheme designed by H. Seide1[5]. The cavity is cylindrical with a moveable bottom, operates in the TE 011 mode and has a Q of 5000. Inside the cavity, two pairs of rods, parallel to the axis and closed by the top of the cavity, form a pair of loops approaching the Helmholtz condition. The loops are terminated by an externa1 loop which couples directly to the tank circuit of an R F oscillator.

The R F oscillator is a gated Colpitts push-pull-circuit, oscillating from 0.5 MHz to 60 MHz in five bands. It uses a VHF QQE03/12 double tetrode. The modulation is accomplished by turning the tube current on and off through a solid state gating circuit. This consists of a switching transistor in the cathode of the tube, driven by a current mode squaring circuit.

The input low frequency (400 Hz) gating signal is sinusoidal. This same signal is fed to the lock-in detector as a reference.

The 10w output is small for most studies at 80°K; however the increase of power results in troublesome R F pick-up.

3. Operation

The operation of the EPR-ENDOR spectrometer is quite simple and is achieved by operations as described below.

1. The klystron is locked to the crystal oscillator simply by varying its reflector voltage;
2. The sample cavity is tuned approximately to the klystron frequency by the moveable bottom. The fine tuning is achieved by manually adjusting the VFO frequency, thus tuning the klystron to the cavity frequency;
3. The VFO locking loop is completed and the local oscillator microwave phase is adjusted until the VFO falls in step with the cavity;

4. The reference signal phase in the 30 MHz detector is adjusted for absorption. This is done by observing the detector output in the oscilloscope and minimizing microphonic noise. The apparatus is then ready to observe EPR;
5. To observe ENDOR the magnetic field is set to an **EPR** line and the microwave power is increased until nearly saturating the electronic transition. The magnetic field modulation is turned off and the R F modulated oscillator is turned on.

4. Experimental Results

The spectrometer sensitivity for **EPR** was determined by observing F-centers in a *KCl* sample at room temperature. The number of F-centers was determined from optical absorption measurements by the well-known Smakula's formula. The EPR observations were made with the cavity described in this article. The sensitivity was found to be 10^{12} AH spins for one sec. time constant.

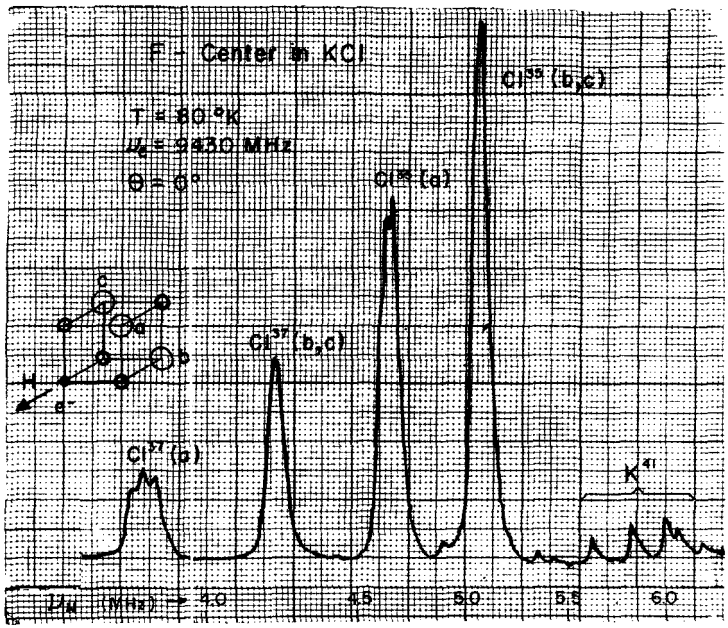

Fig. 2. ENDOR spectrum of F-center in KCl obtained with the spectrornetcr described in *this* paper.

Figure 2 shows an ENDOR spectrum of F-center in KCl at 80° K. The number of centers is approximately 5×10^{17}. The lines due to the 7% abundant K^{41} are clearly seen.

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