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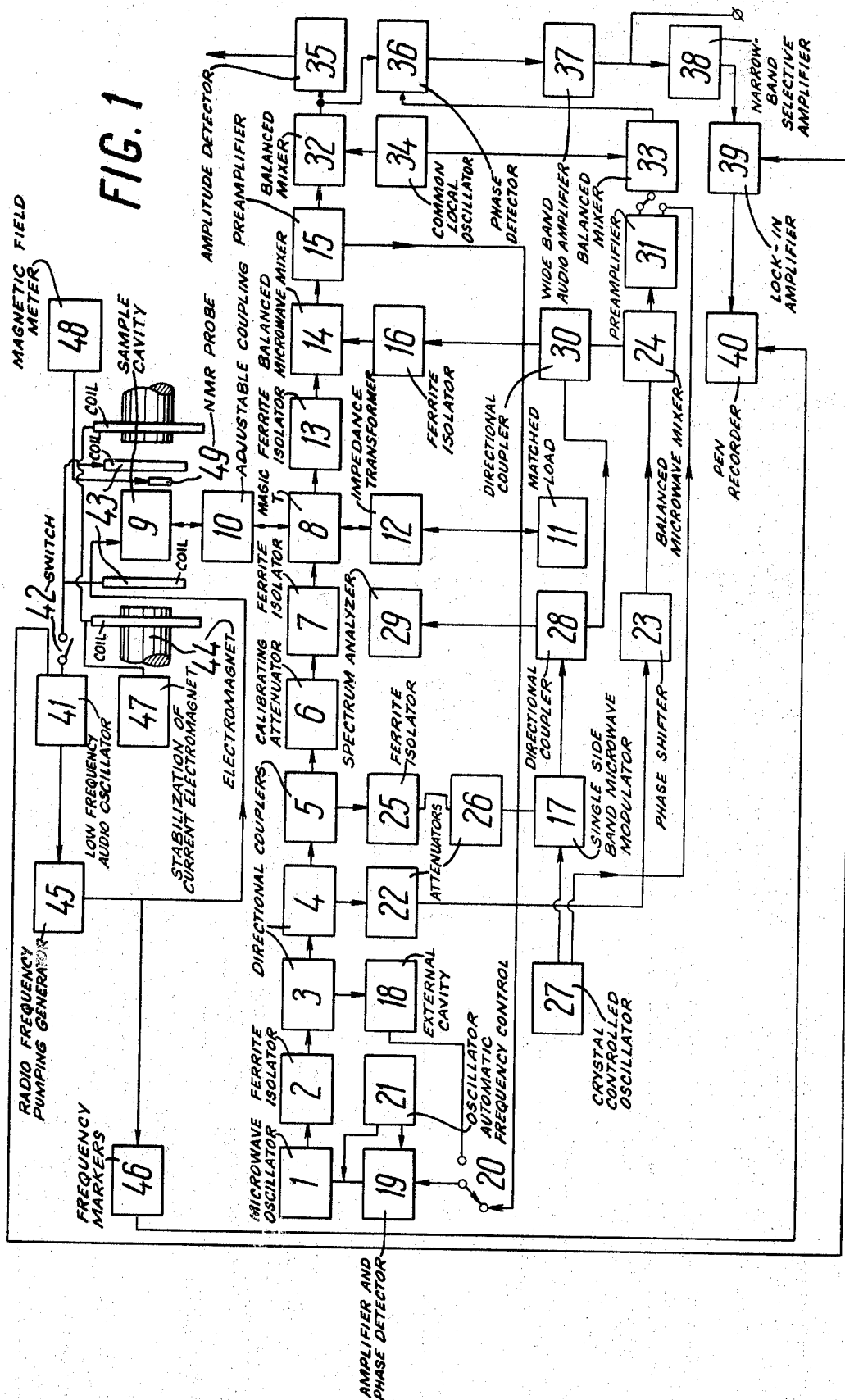
M. A. RUBAN

3,532,965

APPARATUS FOR RECORDING AND OBSERVATION OF THE SPECTRA
OF THE ELECTRON NUCLEAR DOUBLE RESONANCE (ENDOR)

Filed March 24, 1967

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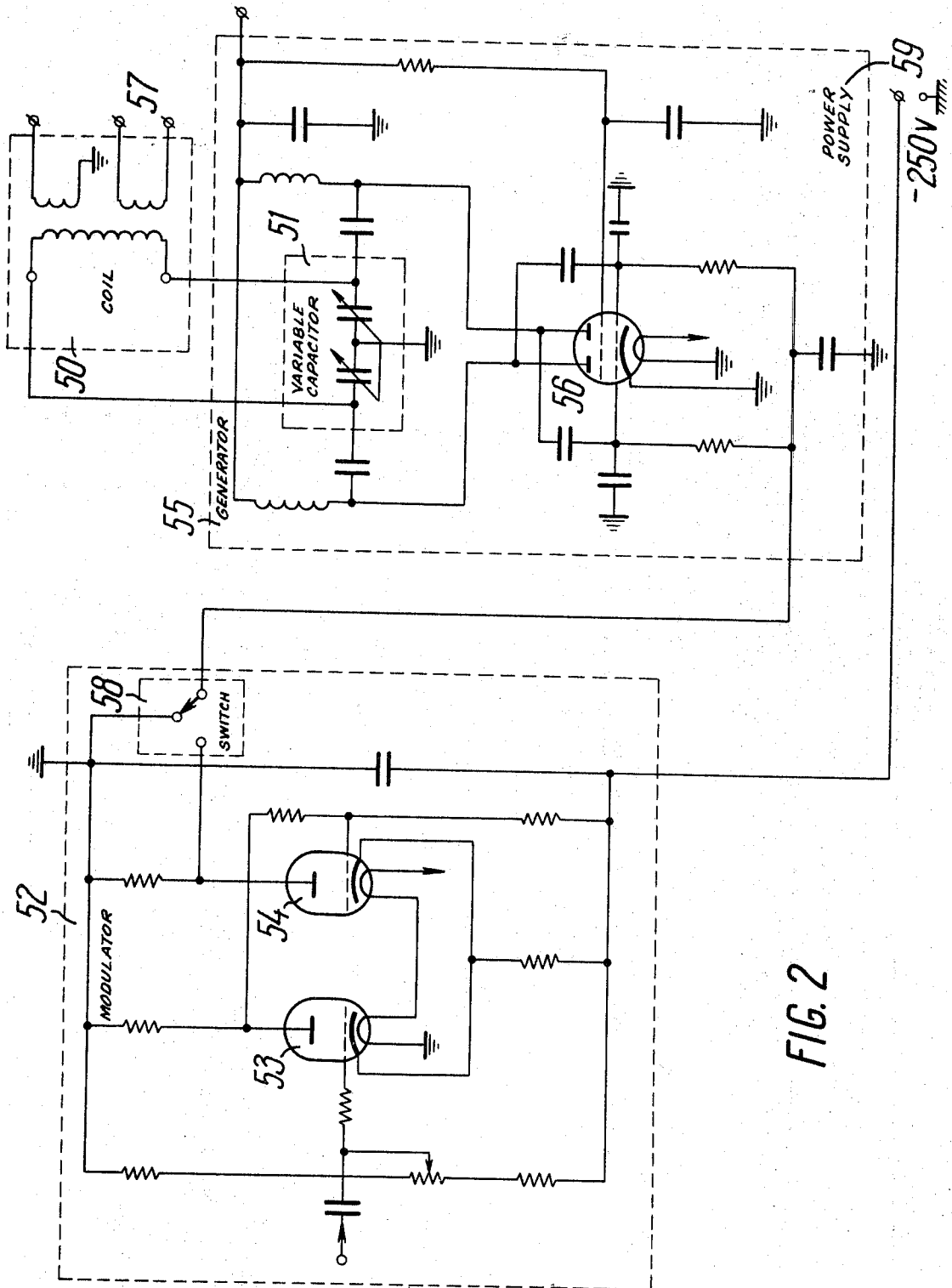


FIG. 2

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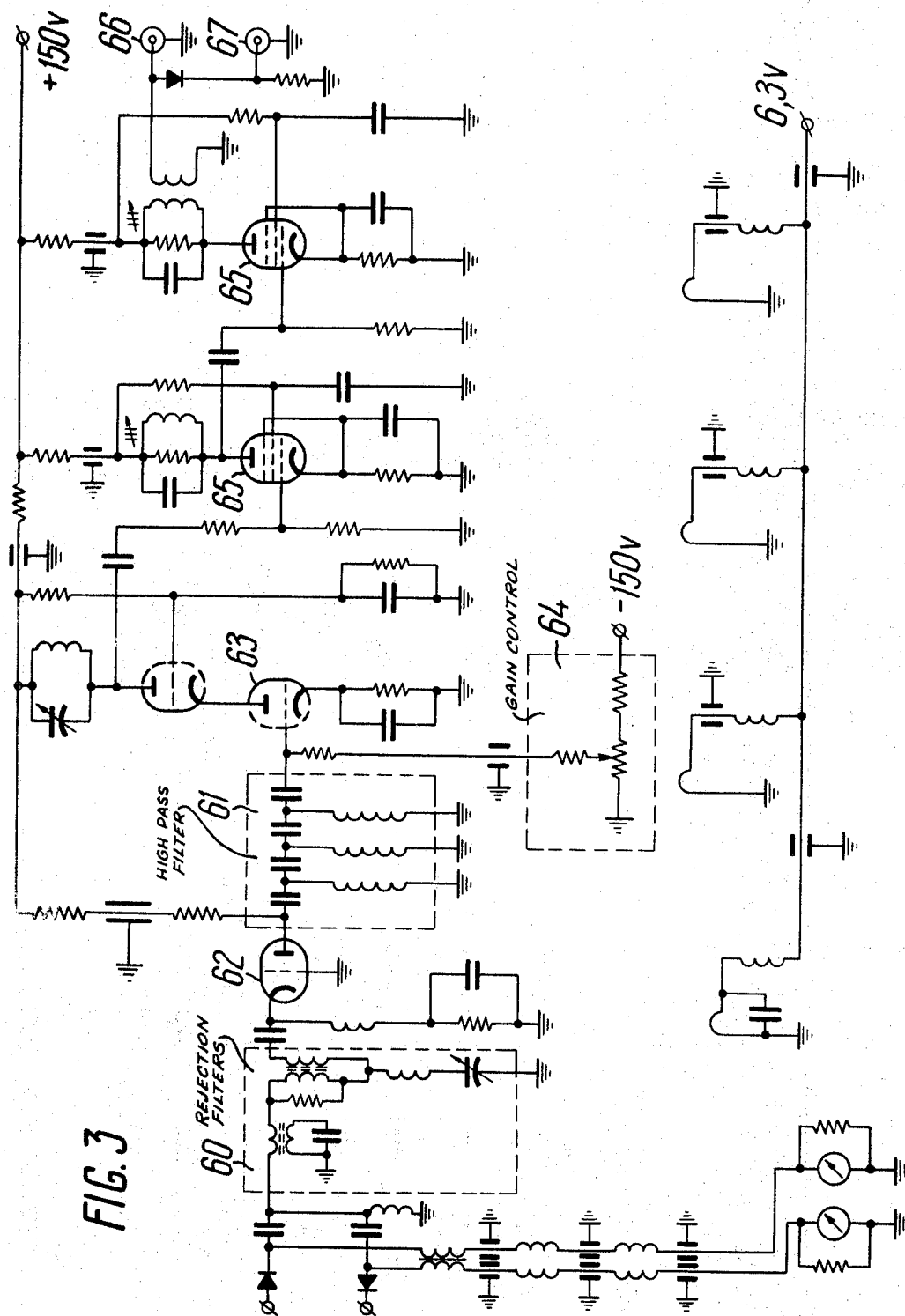
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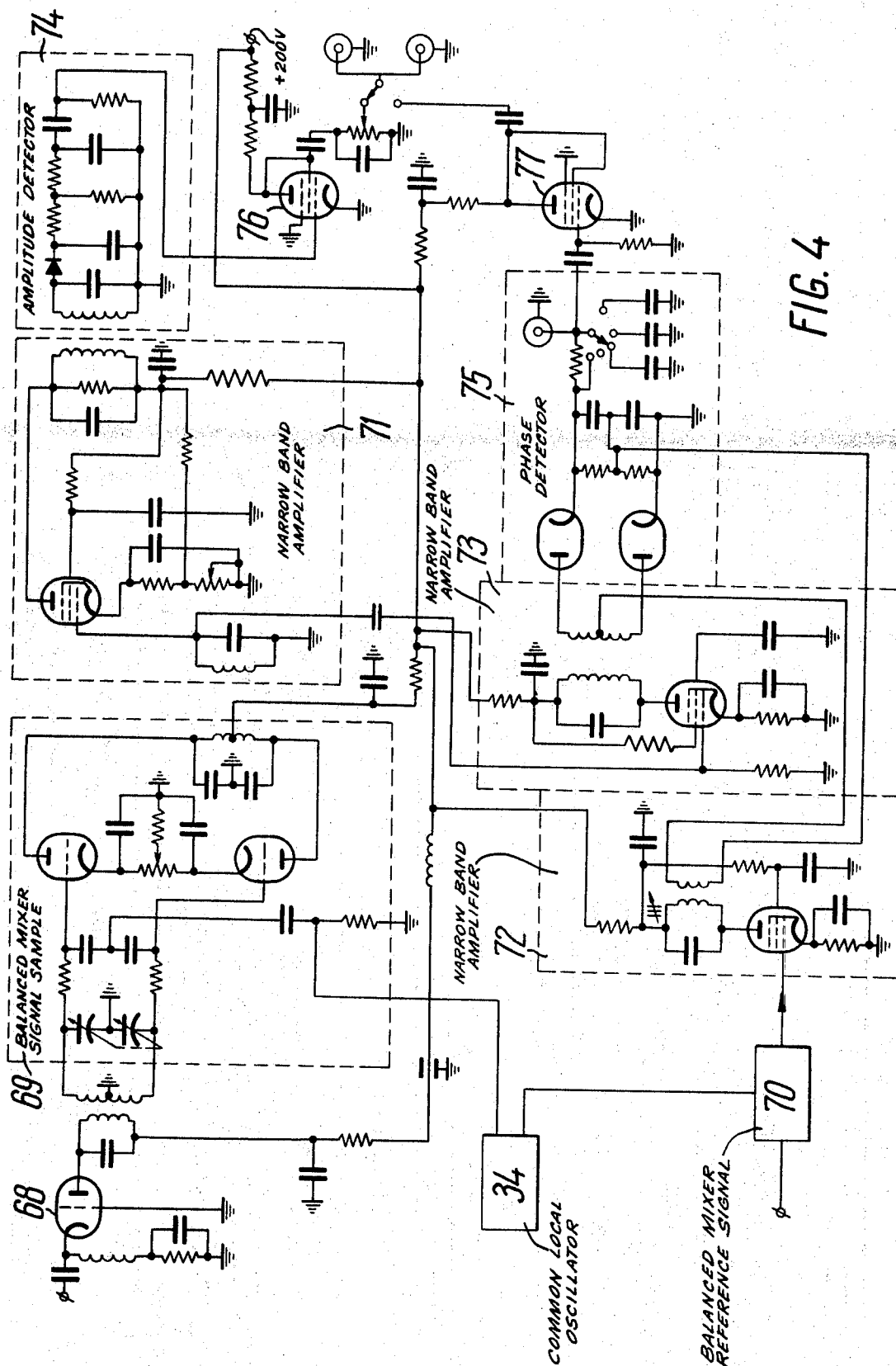
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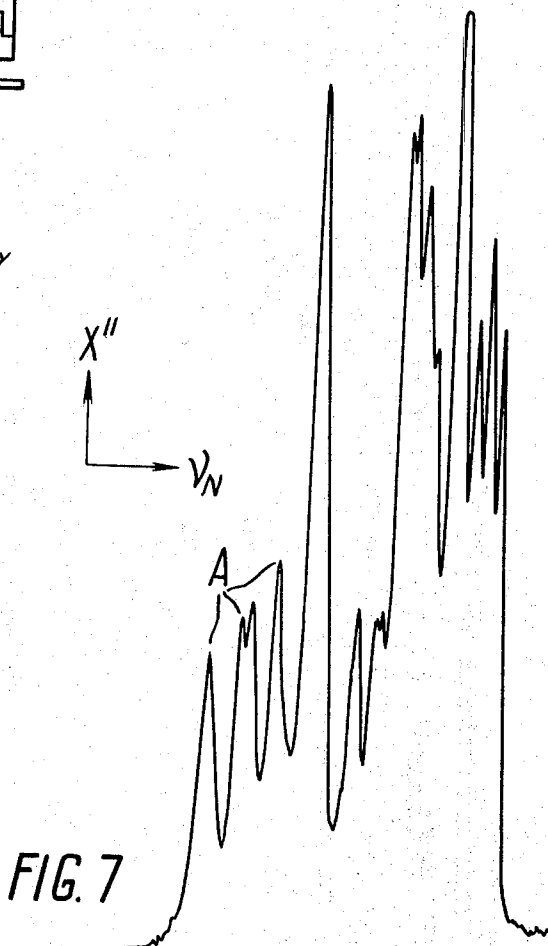
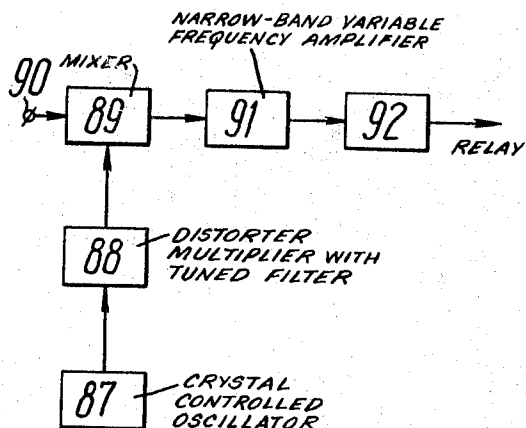
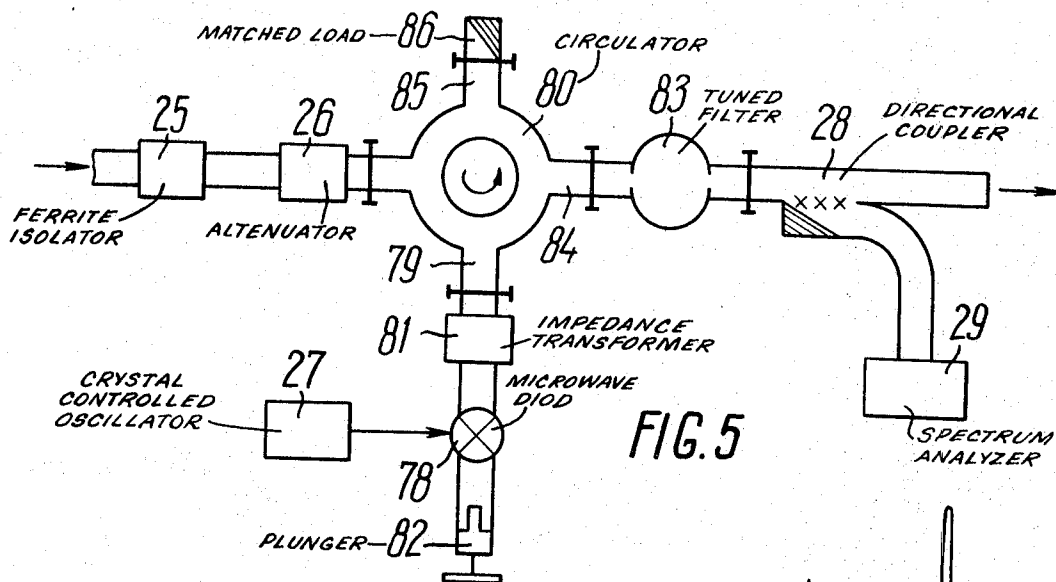
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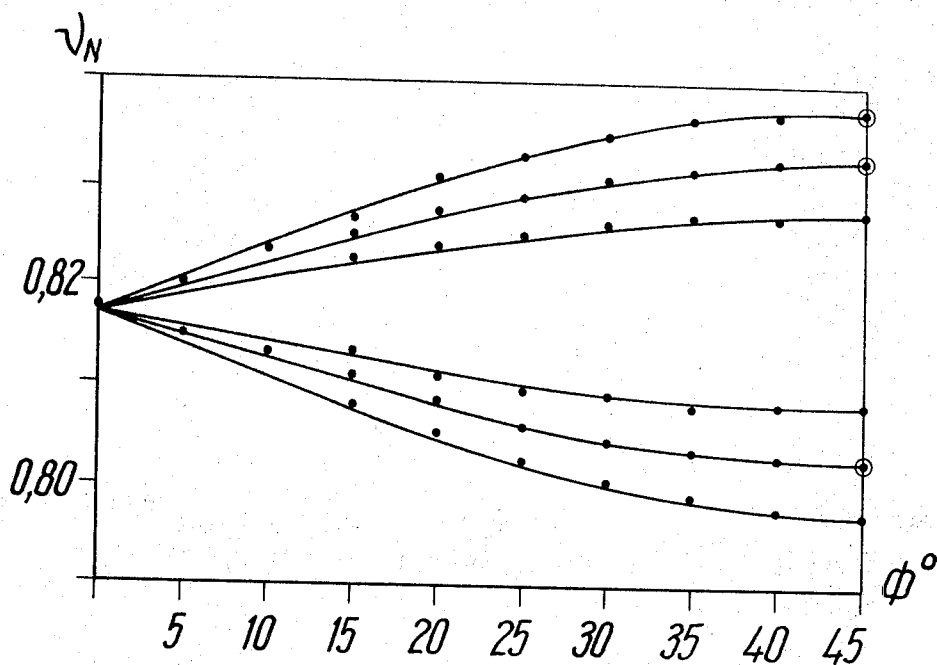


FIG. 8

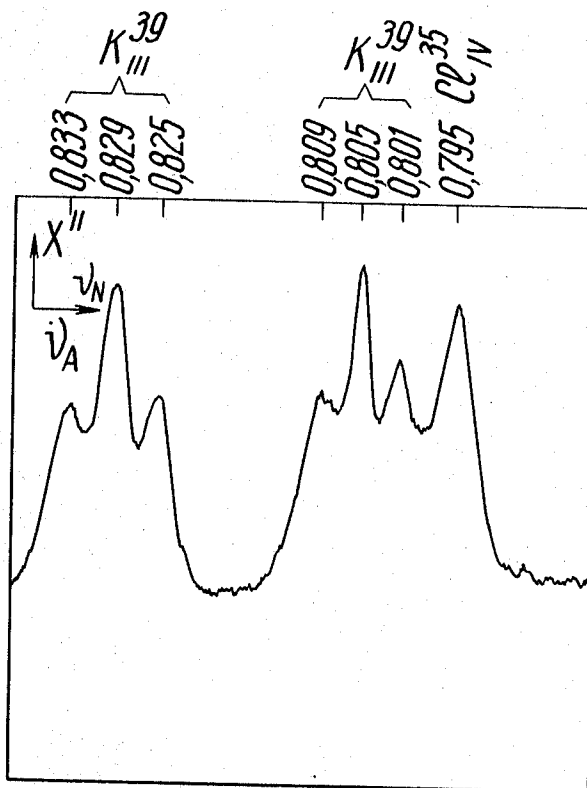


FIG. 9

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APPARATUS FOR RECORDING AND OBSERVATION OF THE SPECTRA OF THE ELECTRON NUCLEAR DOUBLE RESONANCE (ENDOR)

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U.S. Cl. 324—5

4 Claims

ABSTRACT OF THE DISCLOSURE

A system for studying the electron nuclear double resonance (ENDOR), comprising: a superheterodyne EPR spectrometer with a single side band microwave modulator as a local oscillator, wherein an automatic frequency control system enables the spectrometer frequency to automatically track that of the microwave cavity with the sample being investigated or that of the external cavity; a radio frequency pumping oscillator for creating a radio frequency field in the sample with a view to exciting nuclear transitions therein, said oscillator being either continuously (CW) operated, or amplitude pulse-modulated within a wide frequency range, this insuring the possibility of recording dispersion and absorption EPR signals, as well as steady-state and unsteady-state ENDOR signals. The use of the single side band microwave modulator as a local oscillator enables the employment of a narrow-band intermediate-frequency channel whose stability against interferences is additionally enhanced by connecting rejection filters tuned to the subharmonic components of the first intermediate frequency and a high-pass filter at the input of intermediate-frequency amplifiers with the signal from the sample and the reference signal. When recording ENDOR, a system is employed for obtaining frequency markers on the recorded spectra of the electron nuclear double resonance being investigated, whereby the quantitative interpretation of the experimental results is simplified.

This invention relates to apparatus for recording and observation of the spectra of the electron nuclear double resonance (ENDOR) and those of the electron spin resonance (ESR).

A phenomenon of the ENDOR consists in increasing of the prestatuated ESR signal with transitions of the nuclear magnetic resonance saturating, i.e. such transitions are studied in which the orientation of the nuclear spins changes but that of the electron spin remains unchanged.

The known systems for ENDOR study employ an electromagnet with a current stabilization circuit, a sample cavity placed in the gap of said electromagnet, a radio frequency pumping generator, a superheterodyne ESR spectrometer with balanced microwave mixers, intermediate frequency amplifiers and an automatic frequency control system (see Phys. Rev. v. 125, N 1, pp. 89-92, 1962).

The known systems are not sufficiently sensitive, are suitable only for investigations at low (gelium) temperatures due to insufficient power of their radio frequency pumping generators and detect the ENDOR signal by a method of the adiabatic fast passage. Said method is called in literature a method of recording unsteady-state electron nuclear double resonance (ENDOR) and is used mainly for investigating samples with great relaxation times. With this method a signal proportional to the dispersion (x') is recorded. Furthermore, the now existing systems are not sufficiently versatile, since they can detect either only dispersion or absorption signals. A method of recording ENDOR sig-

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nals proportional to the absorption (x''), which is used when investigating samples with short relaxation times is called in literature a method of steady-state ENDOR. Because of the broad bandwidth of their intermediate frequency channel they are more sensitive to interferences from the radio frequency pumping generator. And, finally, the ENDOR spectra being recorded have no frequency markers, which present difficulty as to the handling and use of these spectra.

It is, therefore, an object of this invention to overcome said disadvantages.

It is another object of the invention to provide a versatile high-sensitivity system for study of the electron nuclear double resonance, having good interference-killing feature and high resolution.

With these and other objects in view, in a system for study of the electron nuclear double resonance, comprising an electromagnet with a current stabilization circuit, an UHF sample cavity, placed in the gap of said electromagnet, a radio frequency pumping generator and an electron spin resonance superheterodyne spectrometer with balanced UHF mixers, a preamplifier and a main amplifier of the intermediate frequency, an automatic frequency control and a pen recorder, said radio frequency pumping generator, in accordance with the invention, employs a pulse modulator and a push-pull self-excited oscillator, the grid circuit of which is connected to the pulse modulator and the output circuit is coupled with the UHF cavity to induce a radio-frequency field in the sample.

To preclude the disturbances induced by the radio frequency pumping generator it is expedient to connect rejection filters and a high-pass filter between the output of one of the balanced UHF mixers and the input of the intermediate frequency preamplifier, said rejection filters being tuned to the subharmonic components of the first intermediate frequency. To achieve the same object the main amplifier of the intermediate frequency can be embodied in a circuit including balanced mixers with a crystal-controlled heterodyne and narrow-band amplifiers of the second intermediate frequency, followed by amplitude and phase detectors.

Furthermore, in accordance with the invention, to the output of the radio frequency pumping generator there can be connected a means for measuring frequency and making frequency marks on the electron nuclear double resonance spectrum being recorded, said system being connected to the pen recorder.

The invention will further be better understood from the description of an exemplary embodiment thereof taken in conjunction with accompanying drawings, in which:

FIG. 1 shows a block-diagram of the system for study of the electron nuclear double resonance in accordance with the invention;

FIG. 2 shows a circuit diagram of the radio frequency pumping generator;

FIG. 3 shows a circuit diagram of the preamplifier of the first intermediate frequency;

FIG. 4 shows a circuit diagram of the main amplifier of the second intermediate frequency;

FIG. 5 shows a circuit diagram of the single side band microwave modulator;

FIG. 6 shows a block diagram of the means for measuring frequency and making frequency marks on the electron nuclear double resonance spectrum;

FIG. 7 shows a spectrum of the electron nuclear double resonance for K^{39} nuclei of the first coordination sphere of F-centers in KCl, recorded at room temperature;

FIG. 8 shows an angular dependence of the frequencies of electron nuclear double resonance for K^{39} nuclei of the third coordination sphere; and

FIG. 9 shows a spectrum of the electron nuclear double resonance of the third coordination sphere.

The power from a microwave oscillator 1 (FIG. 1) of the system for ENDOR measurement is delivered through a ferrite isolator 2, a series of directional couplers 3, 4 and 5, a calibrating attenuator 6 and a ferrite isolator 7 to one of the arms of double T-bridge (magic T) 8, one of the arms of which contains a sample cavity 9 provided with an adjustable coupling 10 for balancing of bridge 8 and optimally matching the cavity when the sample is changed. The second arm of bridge 8 is a compensating one and is coupled to a matched load 11 via an impedance transformer 12. Bridge 18 is made massive to decrease microphonics and to increase stability. The input and output arms are provided with ferrite isolators 7 and 13.

An unbalance signal from bridge 8, caused by microwave power absorption by the sample in cavity 9, is fed to a balanced mixer 14 of the electron spin resonance heterodyne spectrometer, said mixer employing a slot hybrid junction and is combined into one unit with a preamplifier 15 for the resulting intermediate frequency. The local oscillator signal is supplied to balanced mixer 14 through a ferrite isolator 16 from a single side band microwave modulator 17.

A directional coupler 3 diverts a part of the power of microwave oscillator 1 to an external cavity 18 by means of which the microwave frequency can be measured with an accuracy of 10^{-4} and to which the microwave frequency may be locked as by means of a frequency modulation system for the investigation of dispersion ESR signals and non-stationary ENDOR signals.

The frequency of oscillator 1 may alternatively be as well automatically locked to the sample cavity 9. In this case an automatic frequency tracking amplifier 19 with a phase detector is connected through a switch 20 to the output of the first intermediate frequency preamplifier 15. A reference voltage for the phase detector of unit 19 and for modulating microwave oscillator 1 is provided from unit 21 oscillator.

Directional coupler 4 diverts a part of the power through an attenuator 22 and a precision phase shifter 23 to form a reference signal via balanced mixer 24 of the electron spin resonance superheterodyne spectrometer a reference signal at the first intermediate frequency for subsequent phase detection purposes.

Directional coupler 5 diverts a part of the power from oscillator 1 via a ferrite isolator 25 and an attenuator 26 to single side band modulator 17, the high frequency voltage for which is supplied from a high frequency crystal-controlled oscillator 27.

A directional coupler 28 is intended for connection of a spectrum analyzer 29.

A directional coupler 30 diverts a part of the power of single side band modulator 17 to balanced mixer 24 for the production of the said reference intermediate signal at the first intermediate frequency. Beyond balanced mixers 14 and 24 the reference and signal channels of the superheterodyne spectrometer are the same in form and comprise respectively first intermediate frequency preamplifiers 15 and 31, balanced mixers 32 and 33 for production of a second intermediate frequency with associated narrow band amplifiers at this the second intermediate frequency, and a common local oscillator 34. The frequency of oscillator 27 is equal to the first intermediate frequency. Therefore as the reference signal there may be used a signal from this oscillator fed to the input of balanced mixer 33 via a switch which is shown in FIG. 1 but not indicated by a reference numeral.

The output signal from the second intermediate frequency amplifier of unit 32 is fed to an amplitude detector 35 and then to an oscilloscope (not shown) or to a phase detector 36 and subsequently to a low-noise wide-band audio amplifier 37, a narrow band selective amplifier 38 and a lock-in amplifier 39 to a pen recorder 40.

A reference low frequency voltage is fed to lock-in

amplifier 39 from a low frequency audio oscillator 41, the low frequency voltage from which is fed via a switch 42 to coils 43 for modulating of the field of an electromagnet 44 when the ESR and the non-stationary ENDOR are being observed. When the stationary ENDOR is being observed the voltage from unit 41 is fed to radio frequency pumping generator 45. Connected to radio frequency pumping generator 45 is a means 45 for measuring its frequency and for introducing frequency markers on the spectrum being recorded, said means being coupled to pen recorder 40 and operating automatically or semi-automatically.

The system also includes a unit 47 intended for stabilization and precise adjustment of the current of electromagnet 44, and a magnetic field meter 48 with a NMR probe 49, placed in the gap of electromagnet 44.

To provide a radio frequency magnetic field intensity sufficient to saturate the nuclear transitions in a sample placed in the microwave sample cavity 9, a radio frequency pumping generator 45 operating over a broad frequency range is employed. Wide-band operation is obtained by switching the coils of the output circuit 50 (FIG. 2) and by means of a variable capacitor 51, whose plates are driven by a synchronous motor with a reduction gear.

The radio frequency pumping generator 45 comprises a Schmidt trigger modulator circuit 52 using valves 53 and 54, and a push-pull self-excited oscillator 55 using valve 56. The oscillator is connected via its grid circuit to the Schmidt trigger. The output circuit 50 of oscillator 55 is inductively coupled through terminals 57 to a radio-frequency pumping loop situated in the microwave cavity.

Generator 45 operates in the pulse modulation mode when a stationary ENDOR signal is being detected and in CW mode when a non-stationary ENDOR signal is being detected. Changing from one mode of operation to the other one is effected by means of a switch 58. The power of oscillator 55 can be adjusted by varying the anode voltage. To obtain a negative modulation pulse from oscillator 55 the cathode of valve 56 is earthed and modulator 52 is supplied from a separate anode voltage supply 59, the positive terminal of which is earthed.

To achieve better interference-killing feature and to suppress the disturbances from radio frequency pumping generator 45, rejection filters 60 (FIG. 3) are connected at the input of first intermediate frequency preamplifier 15, said filters being tuned to subharmonic components of the intermediate frequency, and a high pass filter is connected after the first amplifier stage, said filter providing better input and output matching. The first amplifier stage uses a triode 62 with a grounded grid. The second amplifier stage is connected in a cascade circuit using valves 63 with a gain control unit 64; this stage is followed by a two-stage resonance amplifier using valves 65, the signal from the output 66 of this amplifier being fed to the main amplifier of the first intermediate frequency, and from the output 67 to the automatic frequency correction unit.

The main first intermediate frequency amplifier comprises a high-frequency amplifier using a triode 68 (FIG. 4) with a grounded grid the output, from which is supplied to mixer 69 of identical balanced mixers 69 and 70 for the signal and reference channels respectively, with a common crystal-controlled local oscillator 34, and narrow band amplifiers 71, 72 and 73 for the resulting second intermediate frequency. Narrow band amplifier 71 is followed by an amplitude detector 74, and narrow band amplifier 73 by a phase detector 75, a reference voltage to which is supplied from amplifier 72 of the reference channel.

Main amplifier 32 is followed by low-frequency amplifiers using valves 76 and 77.

Single side band modulator 17, which increases sensitivity of the system and enables a narrow bandwidth of the recording unit to be obtained, uses a microwave

diode 78 (FIG. 5), connected in the arm 79 of a ferrite circulator 80. Connected in front of diode 78 is an impedance transformer 81 for matching diode 78 to the waveguide channel and for suppressing the microwave carrier frequency.

Used to the same purposes is a short-circuiting plunger 82 placed at a quarterwave distance from the plane of diode 78. Discrimination of one of the side frequencies is accomplished with a tuned filter 83, connected at the output arm of ferrite circulator 80. The arm 85 of circulator 80 has a matched absorbing load.

Means 46 (FIG. 1) intended for frequency measurement and for providing markers on the electron nuclear double resonance spectrum consists of a crystal-controlled oscillator 87 (FIG. 6), a distorter 88 (multiplier with tuned filter), a mixer 89, the second input 90 of which is connected to the radio frequency pumping generator 91 and a relay 92 sending a signal to the pen recorder to make a mark.

Operation of the system is based on examination of the electron spin resonance desaturation in the sample with simultaneous saturation of the nuclear transitions. If UHF frequency is fixed, ESR is saturated, the value of the stationary magnetic field is set at the ESR line center, and, under these conditions, the frequency of the radio frequency pumping, which induces saturation of nuclear transitions between different superfine levels, is slowly varied, the spectrum of the ENDOR can be observed. By choosing the frequency ranges of the radio frequency pumping, it is possible to obtain ENDOR spectra of various coordination spheres.

For short time relaxation samples better results are obtained when the stationary ENDOR signal is measured. In this case the spectrometer is adjusted for registering the absorption signal, the automatic frequency correction being made by means of the sample cavity, magnetic field modulation is not used, and a 100 percent amplitude modulation of radio frequency pumping is used with the frequency of said modulation being E_m , which is determined by the condition $Fm \ll 1/\tau$ where τ is the relaxation time of the electron spins. The saturation parameter of the nuclear transitions changes with modulation frequency and the ENDOR signal which can be registered at room temperature changes with the same frequency.

When recording a non-stationary ENDOR signal, the spectrometer is set to record dispersion, the automatic frequency control, which serves to lock the microwave oscillator to the resonance of the external cavity. The magnetic field is modulated at low frequency with some optimum percentage modulation and the radio frequency pumping generator is continuously (CW) operated.

FIG. 7 shows the electron nuclear double resonance spectrum of the first coordination sphere of the F-centers in KCl, recorded at room temperature. The frequency of the radio frequency pumping field was changed in a range from 8 to 14 MHz. Hyperfine structure lines are due to the interaction of the F-center electron with the K^{39} nuclei. A distinct resolution of the quadrupole triplet, lines A, can be seen.

FIG. 8 shows the frequencies of the electron nuclear double resonance of the third coordination sphere (K^{39} nuclei) as a function of the angle. The solid lines show the theoretical curves, the dot, experimental results.

FIG. 9 shows the spectrum of the electron nuclear double resonance of F-centers in KCl for the third and fourth coordination spheres.

A distinct resolution of the quadrupole triplets of the K^{39} nuclei can be seen, the distance between the lines of said triplets being 4 kHz. The investigations and tests of the ENDOR spectrometer show, that the resolution of the order of 1 k.c.p.s. is obtained.

At a liquid nitrogen temperature (78° K.) the ENDOR signals of the F-centers in KCl can be detected with a good signal-to-noise ratio for the fifth, sixth, eighth, ninth

and thirteenth coordination spheres. The obtained data allow very precise determination of the hyperfine interaction constants and consequently of the modulus of the wave function at the corresponding lattice sites.

The system described herein enables normally unresolved the hyperfine structure of the ESR lines to be observed, makes possible the experimental determination of the spatial distribution of the electron wave functions of a single type of atom, e.g. impurity atoms, at the sites of neighbouring atoms at distances up to ten coordination spheres, to investigate the nature and structure of a paramagnetic center, to solve the problems of the structural analysis, to determine the nuclear, spin and quadrupole moments of isotopes, to study nuclear polarization problems, mechanisms of the spin-lattice and spin-spin interaction processes and the like.

The system for ENDOR studies has a resolution which is 3-4 orders of magnitude higher as compared with ESR spectrometers.

The objects of investigation may include the materials having ESR spectra with hyperfine structure. The system makes it possible to investigate non-metallic solids (semiconductors and dielectrics), free radicals paramagnetic ions, metallo-organic paramagnetic complexes, radiation-induced defects and other paramagnetic formation, it may find application in fundamental research in the fields of solid state physics, quantum electronics and structural chemistry.

What is claimed is:

1. A system for study of the electron nuclear double resonance, comprising: a superheterodyne EPR spectrometer including an electromagnet; means for measuring the intensity of the field created by said electromagnet; a system for stabilization of the supply current of said electromagnet; a microwave cavity with a sample placed in the gap of said electromagnet; an external cavity for measuring the microwave frequency of said superheterodyne EPR spectrometer; an automatic frequency control system connected with said external cavity and with the said microwave cavity with the sample and including means such that the microwave frequency of said superheterodyne spectrometer automatically tracks that of the external cavity when recording a dispersion signal of EPR and a signal of unsteady-state ENDOR or that of said microwave sample cavity when recording an absorption signal of EPR and a steady-state ENDOR signal; a microwave oscillator connected with said automatic frequency control system and both with said microwave cavity with the sample for exciting EPR transitions in said sample, and with said external cavity; a single side band microwave modulator connected with said microwave oscillator for obtaining heterodyne power; a crystal-controlled oscillator for obtaining a modulation voltage connected with said single side band microwave modulator for obtaining heterodyne microwave frequency shifted by the value of the frequency of the crystal-controlled oscillator with respect to the initial frequency of said microwave oscillator; a first balanced microwave frequency mixer which is fed with a signal from said microwave sample cavity and with the heterodyne power from said single side band microwave modulator for obtaining a first intermediate frequency; a second balanced microwave frequency mixer which is fed with a signal from said microwave oscillator and with the heterodyne power from said single sideband modulator for obtaining a reference signal at the first intermediate frequency, a first preamplifier which amplifies the output signal of the first balanced microwave frequency mixer and is connected with said automatic frequency control system; a second preamplifier which amplifies the reference signal arriving from the second balanced microwave frequency mixer; main intermediate-frequency amplifiers respectively connected to and adapted to amplify signals arriving from said first and second preamplifiers; an amplitude detector connected with the output of said main inter-

mediate-frequency amplifier connected to the first pre-amplifier for the amplitude detection of the signal from said sample at the intermediate frequency; a phase detector connected with the outputs of the main intermediate-frequency amplifiers; a radio frequency pumping oscillator means which creates a radio frequency field in said sample for exciting nuclear transitions therein; said radio frequency pumping oscillator means including a pulse modulator, a push-pull self-excited oscillator, and switch means connecting said push-pull oscillator both with the said microwave sample cavity for exciting a radio frequency field in said sample, and with said pulse modulator so as to make the amplitude of the radio frequency field in said sample be pulse-modulated when recording steady-state ENDOR signals, and with no pulse-modulation of the amplitude of the radio frequency field in said sample when unsteady-state ENDOR signals are being recorder; and means for recording EPR and ENDOR spectra signals coming from said phase detector and amplitude detector.

2. A system as claimed in claim 1 comprising rejection filters tuned to the subharmonic components of the first intermediate frequency, and a high-pass filter, said rejection filters and high-pass filter being connected between the output of each of said balanced microwave frequency mixers and the input of each of said preamplifiers.

3. A system as claimed in claim 1 wherein said main intermediate-frequency amplifier comprises balanced mixers for the signal from said sample and for the reference signal, respectively, which balanced mixers are con-

nected with a crystal-controlled local oscillator for obtaining a second intermediate-frequency, and narrow-band amplifiers adapted to amplify signals of the second intermediate-frequency.

4. A system as claimed in claim 1 comprising a system connected to the output of the radio frequency pumping oscillator for measuring frequency and applying frequency markers onto the spectrum of the ENDOR signal being recorded, said last-mentioned system being connected with said recording means.

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