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Publication Date
1967-10-01

University of California

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October 1967

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Submitted to: Review of Scientific
Instruments Journal

UCRL-17860
Preprint

UNIVERSITY OF CALIFORNIA

Lawrence Radiation Laboratory
Berkeley, California

AEC Contract No. W-7405-eng-48

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ABSTRACT

An apparatus for the detection of nuclear quadrupole resonance signals using fast sweep techniques that can be operated efficiently over a wide frequency range in a relatively short time is described. The spectrometer utilizes simultaneous lock-in amplification and spectrum accumulation to achieve high signal-to-noise resolution.

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I. INTRODUCTION

Many nuclear quadrupole resonance spectrometers have been described[1-12] in recent years. These rf oscillators and detectors are customarily divided into two categories,[13] regenerative and super-regenerative, depending on their mode of operation.

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1. R. V. Pound and W. D. Knight, Rev. Sci. Instr. 21, 219 (1950).
2. H. G. Dehmelt, Z. Phys. 130, 356 (1951).
3. T. Wang, Phys. Rev. 99, 566 (1955).
4. M. Buyle-Bodin, Ann. Phys. 10, 533 (1955).
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6. C. Dean and M. Pollak, Rev. Sci. Instr. 29, 630 (1958).
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8. R. S. Yamasaki and C. D. Cornwell, J. Chem. Phys. 30, 1265 (1959).
9. J. M. Dereppe and M. Van Meerssche, Bull. Soc. Chim. Belgium, 69, 194 (1960).
10. K. E. Weber and J. E. Todd, Rev. Sci. Instr. 33, 390 (1962).
11. P. M. Bridenbaugh and G. E. Peterson, Rev. Sci. Instr. 35, 698 (1964).
12. R. J. Volpicelli, B. D. Rao and J. D. Baldeschwieler, Rev. Sci. Instr. 36, 150 (1965).
13. This classification does not include techniques where coherent nuclear precession is observed directly, i.e., free induction decay and spin echo-methods.

The most sensitive, the super-regenerative oscillator is primarily used in nqr as a search-type spectrometer since it has typical scan capabilities as high as 5 MHz per hour. There are, however, three distinct disadvantages inherent in this type of instrument. 1) Accurate measurements (±0.1 kHz) of the resonance frequencies are exceedingly difficult and tedious to obtain without resorting to spectrum analyzing techniques.[14] 2) The line shape obtained from a super-regenerative spectrometer bears no analytical relationship to the true line shape; therefore, measurement of the apparent transverse relaxation time, T_2, is impossible while measurement of the spin-lattice relaxation time, T_1, is very difficult. 3) The super-regenerative technique places severe restrictions on the range of both T_1 and T_2 which are necessary for the observation of a nuclear resonance.

This latter point can be demonstrated as follows. In a periodically quenched oscillator the nuclear spins are subjected to bursts of rf field. The oscillator can respond in two ways: 1) the rf power of the oscillator is attenuated by a lowering of the impedance in the LC circuit at resonance, and 2) the voltage induced in the sample coil from coherent nuclear precession changes the characteristic grid bias voltage causing the spectrometer to break into oscillation earlier at resonance. Noise causes the onset of oscillation under non-resonance conditions. It has been suggested,[15] although not clearly demonstrated, that the second mechanism is responsible for the high sensitivity. It seems unlikely that mechanism (1) would

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14. G. E. Peterson and P. M. Bridenbaugh, Rev. Sci. Instr. 37, 1081 (1966).
15. C. Dean (Thesis) Harvard University (1952).

contribute any appreciable sensitivity since it would require that the oscillator be marginal during the rf oscillation cycle. This state is difficult to achieve even under optimum conditions.

Assuming, therefore, that the primary mechanism is (2), it is not difficult to show that $1/T_2$ must be less than the quench frequency[16] for the detection of a nuclear resonance. Furthermore, to avoid saturation the rf field, H_1, cannot be appreciably larger[17] than C $\times$ (quench frequency/$T_1)^{1/2}$ where C is a constant dependent upon the nuclear gyromagnetic ratio, γ, the nuclear spin, I, and the magnetic quantum numbers m and m + 1.[18]

It would, therefore, be desirable to have a system of moderate sensitivity that provides large signal-to-noise ratios, and most important one that is not handicapped by the inherent deficiencies of the super-regenerative method. In addition, it should be capable of reasonable scan rates, e.g., 3-4 MHz per hour. Such a system is described in the remainder of this paper.

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16. This is determined by assuming the voltage induced in the sample coil, v_x, which is proportional to exp $(-T_2{}^2t^2/2)$, at the start of the second quenched oscillation, i.e., t = 1/quench frequency is 10% of its value at t = 0.

17. T_2 is replaced by 1/quench frequency in the equation for saturation, i.e., $H_1 > C \times (1/T_1T_2)^{1/2}$.

18. T. P. Das and E. L. Hahn, Nuclear Quadrupole Resonance Spectroscopy, (Academic Press, New York, 1958).

II. FAST SWEEP SPECTROMETER

The spectrometer described is a frequency modulated regenerative oscillator with sweep capabilities of 20-80 kHz per second in 100-500 kHz increments from 5-50 MHz. The circuit in Fig. 1 is a modified Colpitts[19] oscillator followed by an audio-amplifier identical to that used by Gutowsky et al.[20]

An excellent analysis of the autodyne circuit as applied to EPR has been given in a review article by Bruin[21] and for NMR by Roberts.[22] The principles are the same for nqr.

The rf energy absorbed by the sample at resonance lowers the oscillation amplitude by lowering the LC impedance of the tank circuit. This change manifests itself as an increased audio-component at the modulation frequency. After audio-amplification the signal is detected by a phase sensitive narrow banded amplifier, a PAR HR-8 lock-in amplifier. Because the frequency is being swept at such a high rate, it is necessary to use a very low RC time constant (10-100 msec) in the lock-in. The high rate of sweep, e.g., 50 kHz per second, accomplishes two purposes. First, it prevents saturation of the nqr resonance under saturation conditions, $H_1 > 1/\gamma\,(T_1T_2)^{-1/2}$, provided the passage through resonance is less than T_2.

19. E. V. Malmstadt, C. G. Enke and E. C. Toren, Jr., Electronics for Scientists (W. A. Benjamin, Inc., New York, 1963).
20. H. S. Gutowsky, L. H. Meyer and R. E. McClure, Rev. Sci. Instr. 24, 644 (1953).
21. F. Bruin, Advances in Electronics and Electron Physics (Academic Press, New York, 1961), Vol. 15.
22. A. Roberts, Rev. Sci. Instr. 18, 845 (1947).

Secondly, it allows one to efficiently time-average the signal output from the lock-in amplifier (see Fig. 2). This increases the overall sensitivity from the lock-in by the $\sqrt{n}$ where n is the number of sweeps through resonance. Allowing time for manual readjustment of the oscillator level every 200-500 kHz, the spectrometer is capable of scanning 3-4 MHz every hour.

In principle large signal-to-noise ratios can be obtained in phase-sensitive detection methods using slow sweep rates and long time constants, e.g., 1 kHz per minute and 3 seconds or longer. This assumes, however, that saturation is not a problem at these slow sweep rates. In practice, the signal-to-noise ratio is not a linear function of the square root of the time constant. As shown in Fig. 3, at a given value of the lock-in amplifier time constant, characteristic of each instrument, the signal-to-noise ratio becomes nonlinear until a plateau is reached at some value. This is primarily due to the increased low frequency noise component[23] in the nonlinear region. For most marginal and super-regenerative oscillators the nonlinearity begins at a time constant on the order of 1-10 seconds. Analog or digital averaging on the other hand are linear to infinite "effective time constants", i.e., number of repetitive sweeps.

When signal recovery requires long characteristic time constants, as is generally the case in nqr, it is better to decrease the lock-in detection time, increase the frequency sweep rate, and analog or digitally average repetitive sweeps.

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23. M. P. Klein and G. W. Barton, Jr., Rev. Sci. Instr. 34, 754 (1963).

In order to simultaneously frequency-modulate and frequency-sweep two varactor bridges, B_1 and B_2, are connected across the tank circuit. It is important to DC bias[24] both bridges so that the varactors operate in their low capacitance region. In this manner the circuit Q is high and not limited by the lower varactor Q at low voltages.

The oscillator is frequency-modulated by a DC biased 1 volt (peak-to-peak) 200 Hz per second sine wave across B_1. An Exact Model 250 waveform generator supplies the ramp voltage, 30-50 volts, necessary for frequency sweeping at B_2. It also triggers a DC coupled PAR-TDH-9 Waveform Educator which serves as an analog memory in which the signal is accumulated. Single sweep and an accumulate spectra are illustrated[25] in Fig. 4. In both cases the accumulated signal-to-noise ratios are comparable to those observed in a high power super-regenerative spectrometer[26] operated under optimum conditions.[27]

The rf frequency is continually monitored by a HP 5245L frequency counter. Two turns of insulated wire wrapped around the "hot" terminal

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24. The value of the DC bias across B_1 and B_2 apply only to Microwave Associates Type MA-4273C and MA-4273E varactors respectively.
25. Mn^{55} resonances recently found, in this laboratory.
26. C. B. Harris, unpublished work.
27. The conditions were adjusted such that both the marginal and super-regenerative oscillator could search 4 MHz in one hour. The super-regenerative lock-in amplifier time constant was 3 seconds.

of C serves as an effective antenna. Utilizing an HP 5261A video amplifier the rf level can be conveniently set such that the oscillator operates at optimum marginality, e.g., about 1 millivolt on the HP 5261 A. The disadvantage of such a monitor system is that the antenna introduces stray capacitance in parallel with the tank circuit. This has the effect of lowering the Q about 5-10%. Such a loss, however, does not visibly decrease the overall sensitivity of the instrument.

To insure adequate shielding against radio stations and spurious rf signals, the sample coil, the rf oscillator, and the audio-amplifier are placed in three compartments of a brass box.

Finally, a simple method has been devised for measuring the resonance frequency and half-width. When the ramp voltage at B_2 is used to sweep a storage oscilloscope in the external horizontal mode and the PAR TDH-9 readout is used as the signal input, oscilloscope becomes the x-y in frequency and amplitude respectively. When a sufficient signal has accumulated in the analog memory, one replaces the ramp voltage with a manually adjustable DC bias and simply centers the CRT electron beam at the appropriate position on the x-axis and reads the frequency from the frequency counter. Accuracy of ±0.1 kHz can easily be obtained in this manner.

ACKNOWLEDGEMENTS

This work was supported by the United States Atomic Energy Commission under the Lawrence Radiation Laboratory, Inorganic Materials Research Division, Berkeley, California.

We wish to express our appreciation to R. J. Myers for many helpful discussions.

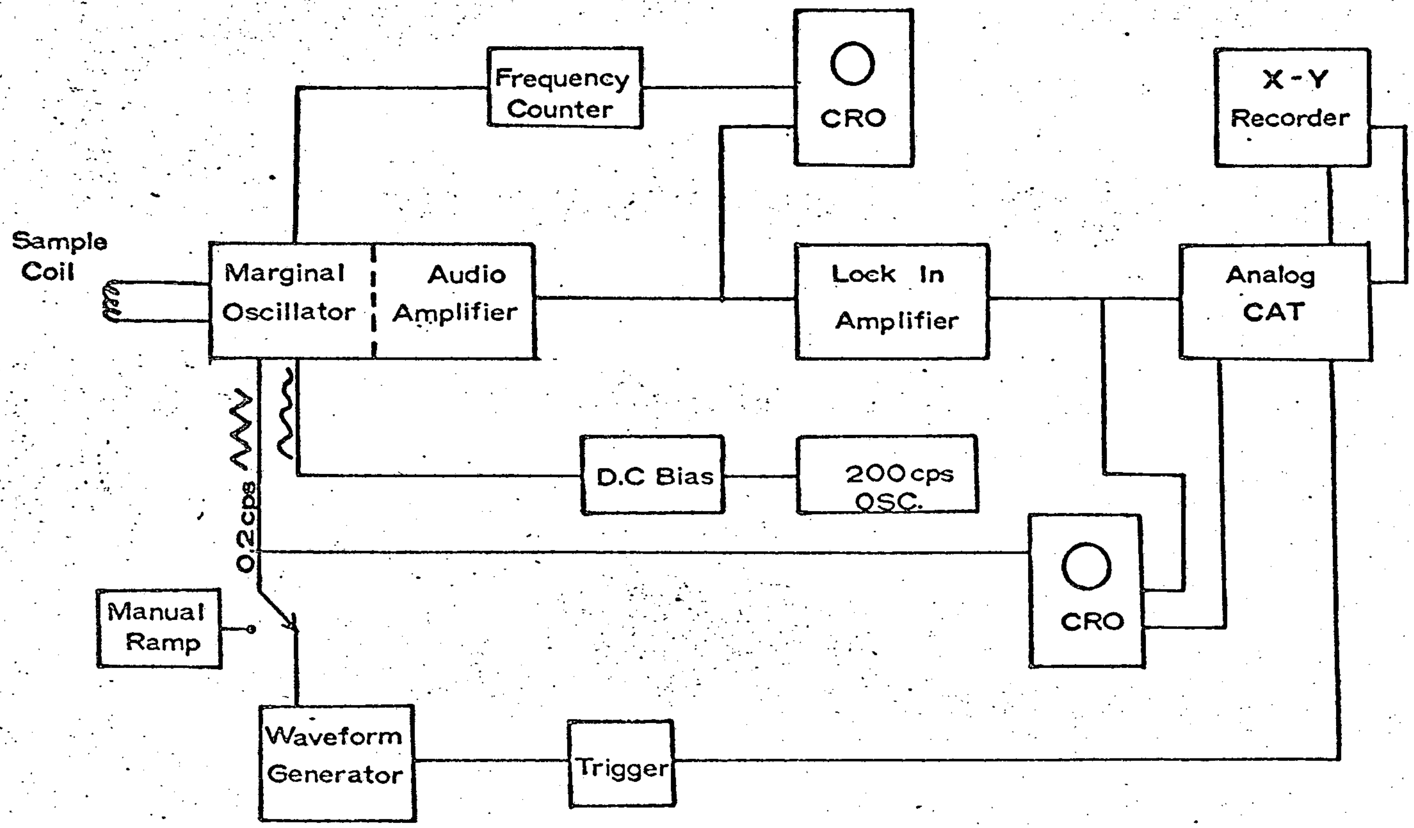
FIGURE CAPTIONS

Fig. 1 Block diagram of the fast sweep nqr spectrometer.

Fig. 2 Circuit diagram of the marginal oscillator and audio amplifier: C = 140 μμf; C' = 325 μμf; C" = 2-11 μμf; C"' = 50 μμf; all other capacitance in μf.

Fig. 3 Signal-to-noise increase versus $\sqrt{\tau}$. τ equals the lock-in amplifier time constant for —— and the number of repetitive sweeps for - - - - .

Fig. 4 (a) Single sweep Mn^{55} nqr spectra of (C_4H_4N) Mn $(CO)_3$. (b) 25 sweeps-accumulated Mn^{55} nqr spectra of (C_4H_4N) Mn $(CO)_3$. (c) Single sweep Mn^{55} nqr spectra of $(C_{12}H_9O)$ Mn $(CO)_3$. (d) 25 sweeps-accumulated Mn^{55} nqr spectra of $(C_{12}H_9O)$ Mn $(CO)_3$. In all cases the sweep rate was 20 kHz per second. Spectra (a) and (b) are spectra of a relatively strong signal. (c) and (d) are spectra of a very weak signal. The latter pair can barely be resolved by super-regenerative techniques.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CRO
X - Y Recorder
Sample Coil
Marginal Oscillator
Audio Amplifier
Lock In Amplifier
Analog CAT
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CRO
Manual Ramp
Waveform Generator
Trigger

Fig. 1

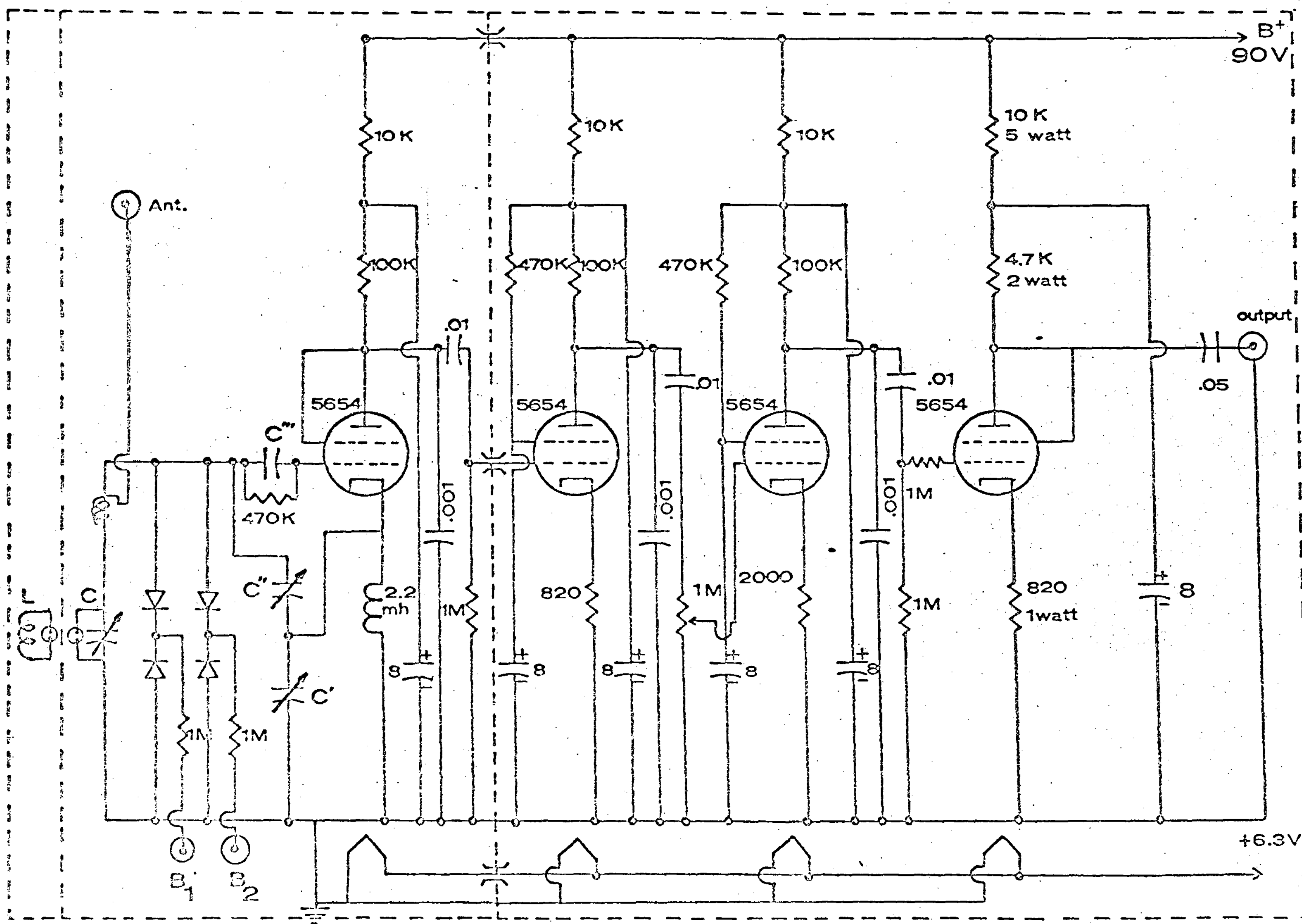
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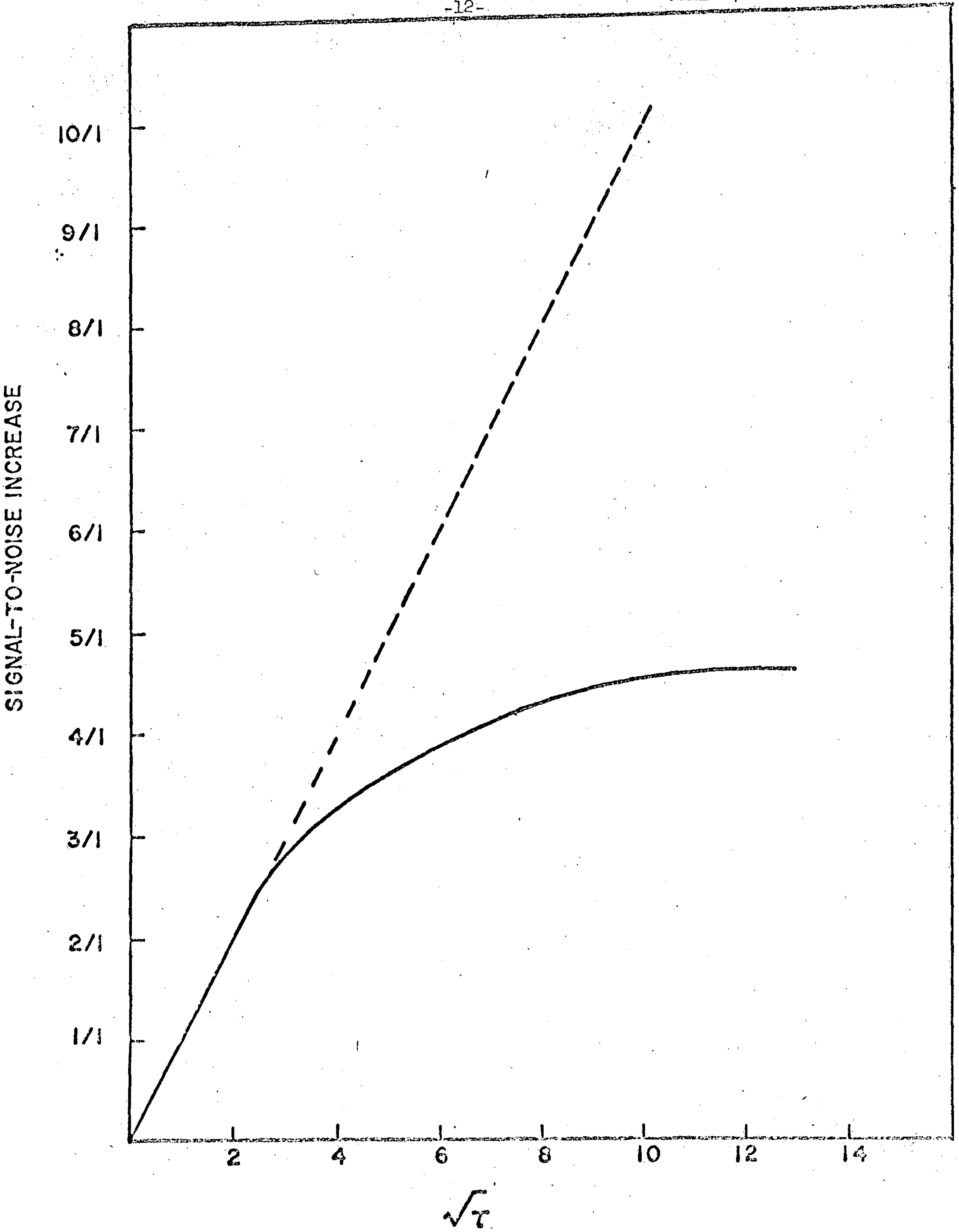
Fig. 2


SIGNAL-TO-NOISE INCREASE
10/1
9/1
8/1
7/1
6/1
5/1
4/1
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2/1
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2
4
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14
$\sqrt{\tau}$

Fig. 3

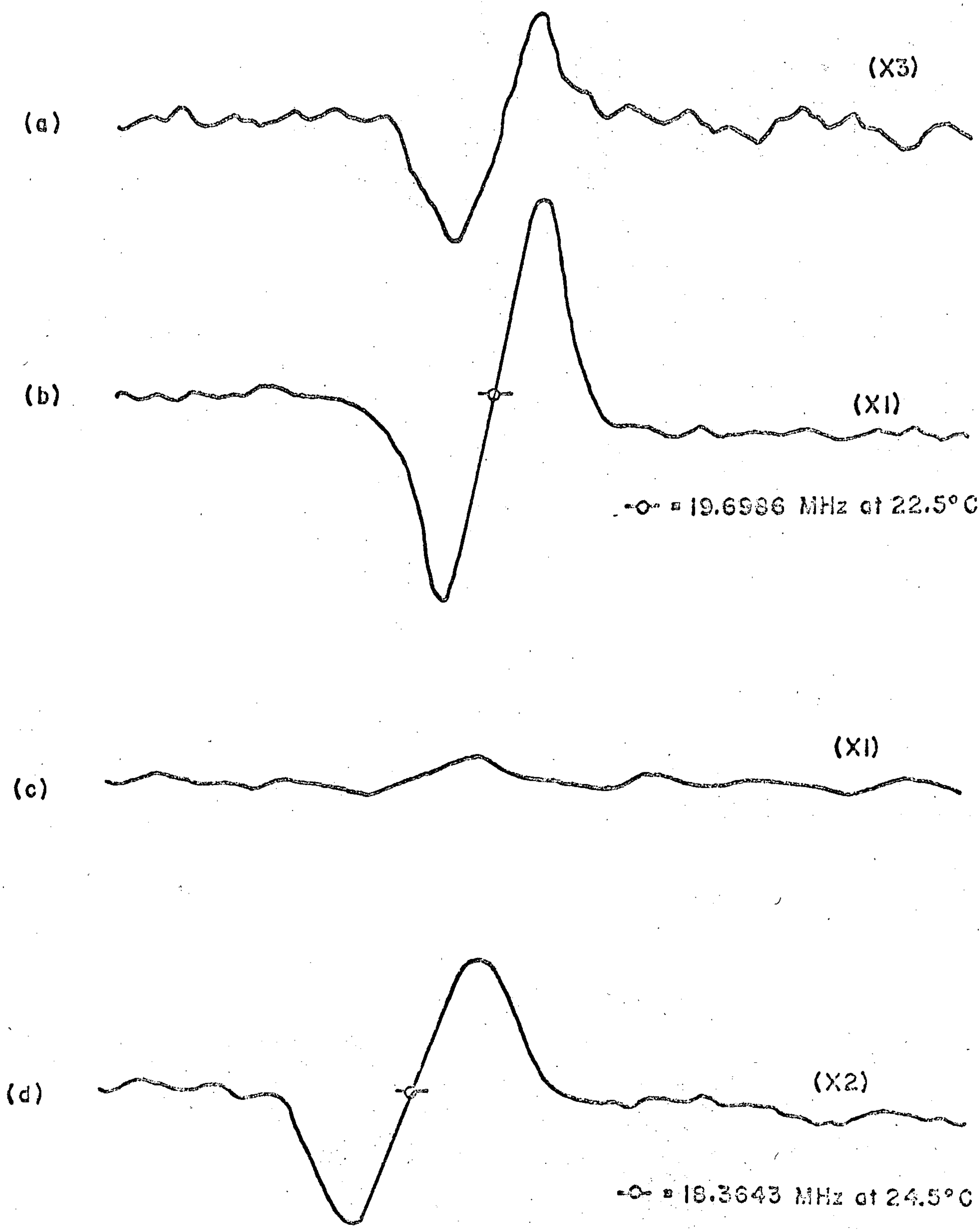

Fig. 4