NBS TECHNICAL NOTE

344

A Sensitive Recording NMR Ultrasonic Spectrometer

LAWRENCE W. JAMES

U.S. DEPARTMENT OF COMMERCE
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A Sensitive Recording NMR Ultrasonic Spectrometer

Lawrence W. James*

Instrumentation is described for automatically obtaining a continuous recording of ultrasonic absorption lines. Ultrasonic power is added to the crystal lattice by a transducer mounted on a single crystal of the sample. The interaction of the ultrasonics with the nuclear spin system is recorded by using a pulse NMR system in conjunction with a boxcar integrator. This technique is more sensitive and provides more easily interpretable results than earlier systems.

1. Introduction

The first experimental work in measuring the effect of ultrasonic power on the nuclear spin system in solids used a pulse NMR system. The effect of the ultrasonics on the nuclear spin system was determined by the difference in signal height which was observed on an oscilloscope when the ultrasonic power was present and when it was absent [Proctor, and Tanttila, 1956; Proctor and Robinson, 1956]. Measurements of the ultrasonic absorption linewidth were obtained by making a number of separate measurements at frequencies on either side of the transition frequency.

Direct observation [Menes and Bolef, 1958; Bolef and Menes, 1959] of the absorption of phonons by the nuclear spin system has been made by using a transducer bonded to a mechanically resonant sample as the varying impedance in the tank circuit of a marginal oscillator. A modulated magnetic field, phase detector, and recorder were used to obtain a recording of the derivative of the absorption line as the nuclear

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Larmor frequency was swept through the oscillator frequency. This technique offers the advantage of a continuous recording, but has the disadvantages of requiring more refined ultrasonic techniques, of limiting the voltage which could be applied across the transducer to a fairly narrow range, and of being considerably less sensitive than the indirect pulse NMR technique.

This paper describes a system using the pulse NMR technique which automatically records a continuous plot of the ultrasonic absorption line. From this plot, the linewidth, the line shape, and any unusual effects may be easily observed. Other advantages of this system are its ability to record directly the absorption line rather than its derivative, its ability to detect an effect too small to be seen with the normal pulse NMR system, and its ability to observe a saturation in samples with long spin-lattice relaxation time, T_1.

2. Experimental Equipment

A block diagram of the entire system is shown in Fig. 1. The pulse transmitter and receiver form a conventional pulse NMR detection system. The ultrasonic rf amplifier is a three-stage tuned amplifier which boosts the low voltage output of the variable frequency oscillator (VFO) to a variable voltage of up to 500 volts which may be applied across the transducer. The output frequency is the same as the VFO frequency; no multiplication is used. An automatic level control is added to keep the output voltage constant within 1% over a wide frequency range without the need for retuning. The relay is present to short out the receiver input while the ultrasonic power is applied.

The heart of this system is the boxcar integrator. This device contains an RC integration network and a gate which applied the signal to the integration network only during a sampling pulse. The sampling

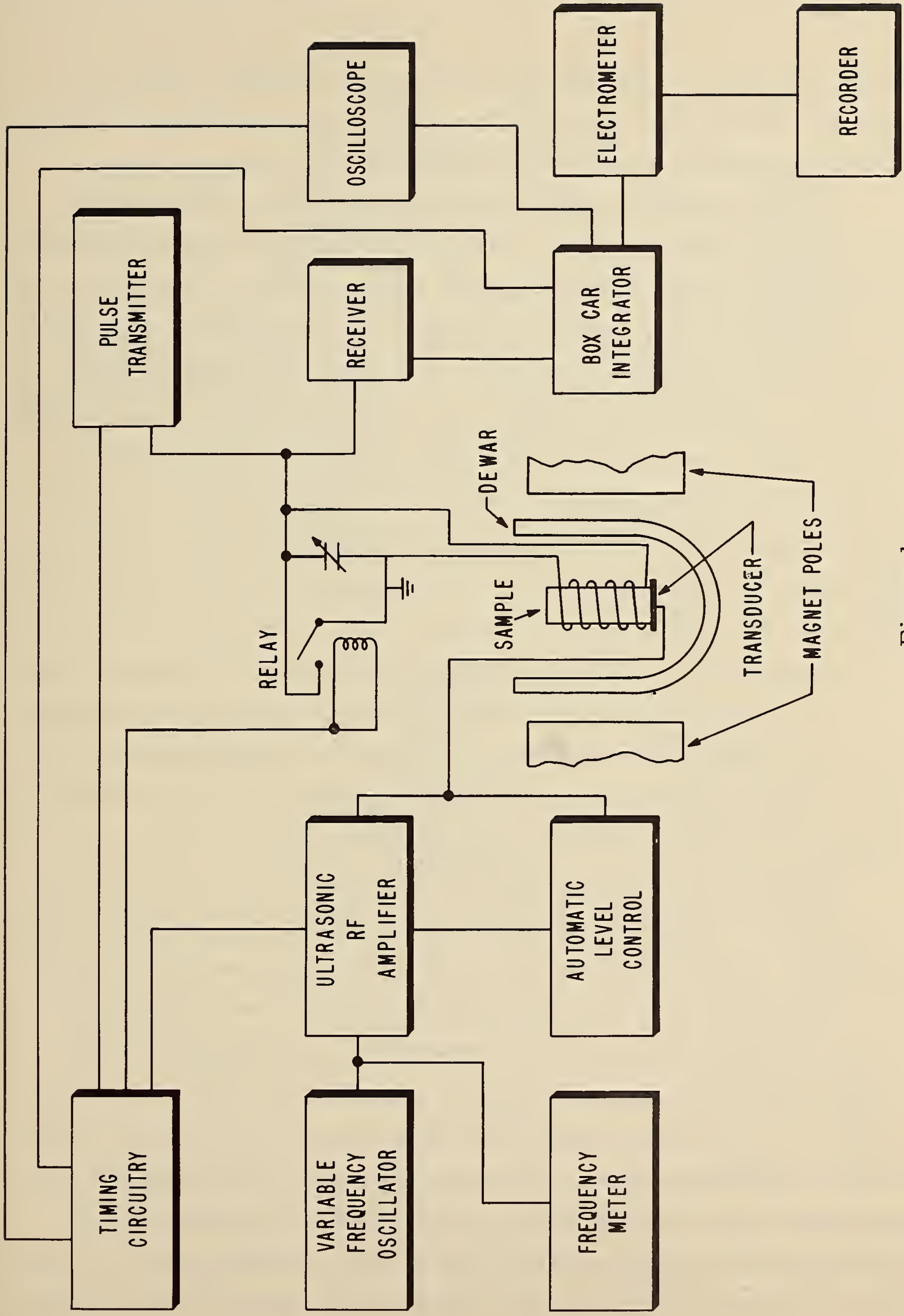

TIMING CIRCUITRY
VARIABLE FREQUENCY OSCILLATOR
FREQUENCY METER
ULTRASONIC RF AMPLIFIER
AUTOMATIC LEVEL CONTROL
RELAY
SAMPLE
TRANSDUCER
MAGNET POLES
DEWAR
PULSE TRANSMITTER
RECEIVER
BOX CAR INTEGRATOR
OSCILLOSCOPE
ELECTROMETER
RECORDER

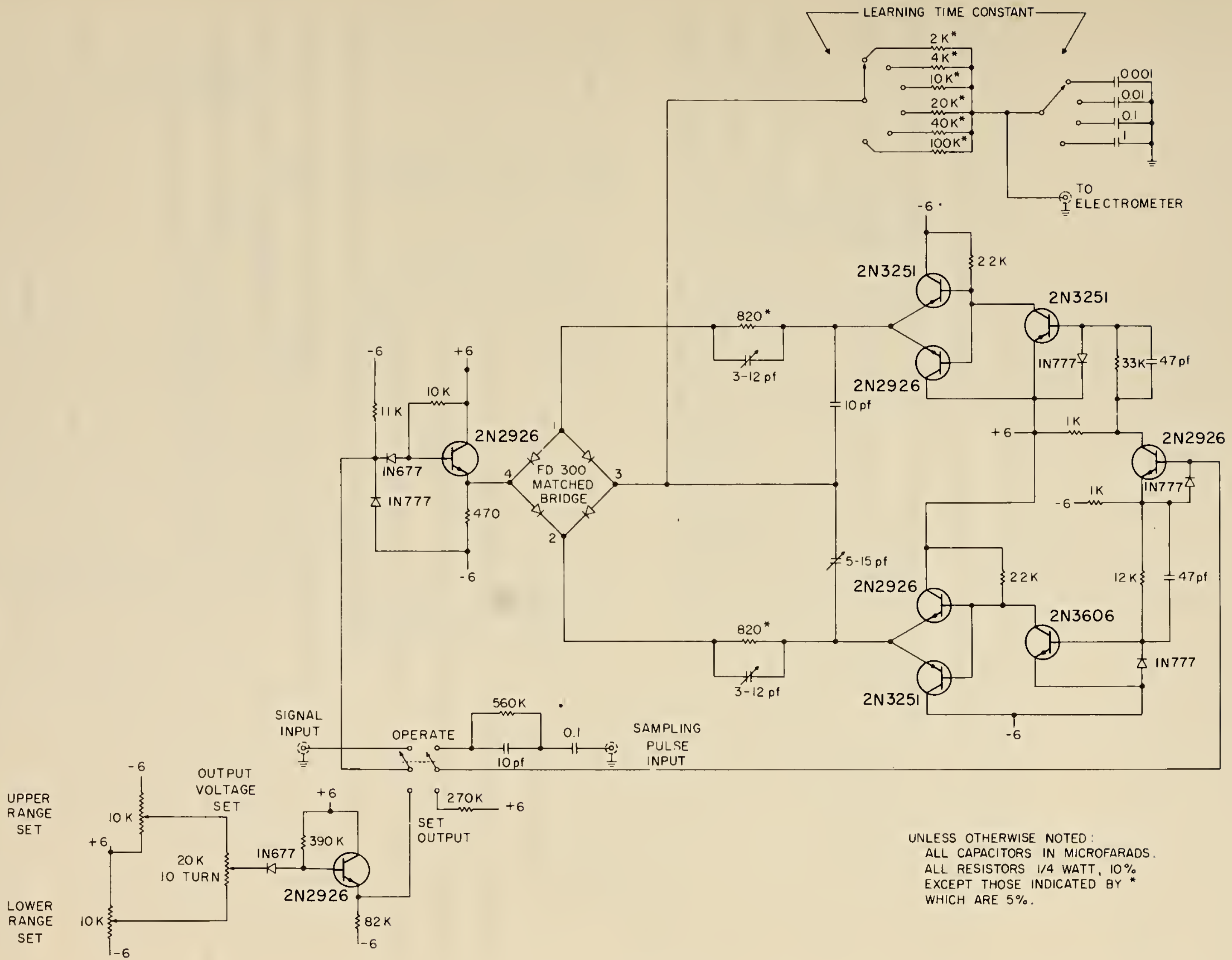
Figure 1

pulse is timed to occur when the NMR signal is present. When the sampling pulse is not present, the voltage across the capacitor remains constant except for a very small drift caused by leakage current.

A circuit diagram of the boxcar integrator developed in this laboratory is shown in Fig. 2. With the set output switch in the operate position, the signal is fed through the emitter follower input stage into the diode bridge gate. When no sampling pulse is present, none of the diodes in the bridge are conducting. When a pulse is applied to the sampling pulse input, symmetric pulses of opposite polarity are applied to terminals 1 and 2 of the diode bridge, causing all four diodes to conduct and feeding the signal into the RC integration network. The diode bridge contains matched, ultra-low-leakage diodes. The three trimmers are adjusted for minimum coupling of the leading and trailing edges of the sampling pulse to the integration network input. The circuit is designed for a 25-volt sampling pulse and a ±3-volt signal range.

All signal circuits including those in the receiver are dc coupled and compensated for temperature drift. The dc coupling is necessary to prevent any signals not occurring at the same time as the sampling pulse from having an effect on the integrator output.

The integrator time constant, referred to as the "learning time constant," is variable by switching both resistors and capacitors in the integrator. Low leakage switches and mylar capacitors are mounted in a sealed box to prevent accumulation of dirt. If the learning time constant is short compared to the length of the sampling pulse, the voltage across the capacitor after the sampling pulse will correspond closely to the average voltage of the signal which was present near the end of the sampling pulse. If the learning time is long compared with the length of the sampling pulse, the voltage will correspond to the average signal voltage during the last several sampling pulses. In this way, variations in signal height caused by noise during each sampling



UNLESS OTHERWISE NOTED:
ALL CAPACITORS IN MICROFARADS.
ALL RESISTORS 1/4 WATT, 10%
EXCEPT THOSE INDICATED BY *
WHICH ARE 5%.

Figure 2

pulse will be averaged out. For a discussion of the advantage in signal-to-noise ratio that may be obtained by integrating over several sampling pulses, see the article by Dwight O. North [1963].

3. Experimental Technique

The sequence of operations is shown in Fig. 3. This sequence is repeated continuously at time intervals somewhat longer than T_1. The boxcar integrator output corresponds to the average signal height during the sampling pulse. The sampling pulse is timed to occur near the peak of the signal for the best signal-to-noise ratio. The VFO is set to a frequency on one side of the resonance frequency and swept through the line by a motor drive. As the NMR signal is reduced by the ultrasonic phonons, the recorder will follow this reduction and a recording of the line will be obtained.

Some precautions are necessary to insure the successful operation of this system. The sweep rate must be slow enough so that the frequency swept between sampling pulses is an incremental part of the linewidth. Well regulated power supplies must be used to insure stability of the height of the NMR signal during the period of time necessary to record the line. It is also desirable to synchronize the timing cycle with the power line frequency so that any 60-Hz noise which is present will be identical for each sampling pulse. The ultrasonic voltage must be adjusted so that the NMR signal is not completely saturated when the ultrasonic frequency is at the resonant frequency to avoid flattening of the peak of the absorption line.

For use with a good signal-to-noise ratio and a large percentage of saturation, the learning time constant is adjusted to 30 to 50 per cent of the sampling pulse length so that changes in average signal height will be followed on each pulse. Two samples of absorption lines in this

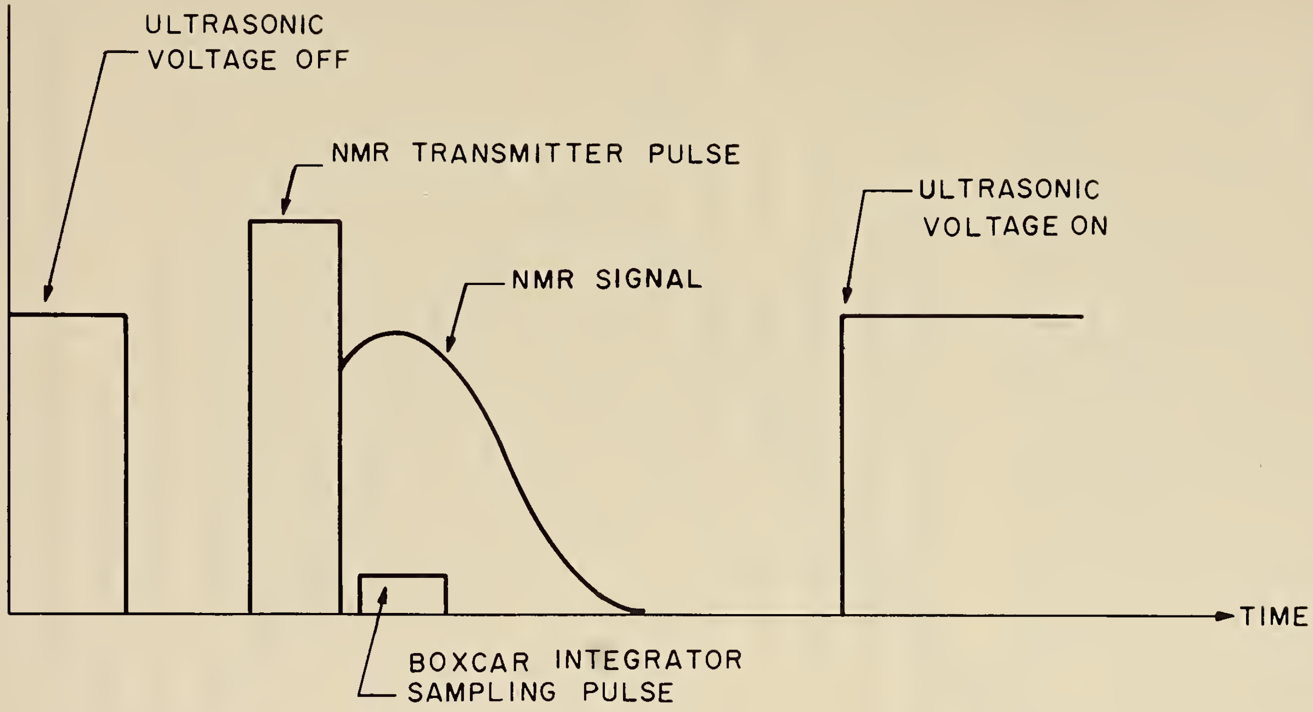


Figure 3

Sequence of Operations

category are shown in Figs. 5 and 6. Figure 4 shows the In^{115} and In^{113} resonances in InSb. Figure 5 is a dual resonance of Sb^{121} and Ga^{69} in GaSb. Both of these curves were obtained using single crystals at liquid nitrogen temperature. The NMR system was at 7.5 MHz and the ultrasonic energy was at 15 MHz to induce $\Delta m = \pm 2$ transitions. Approximately twenty minutes were required to record each trace. In this period of time, the signal was sampled approximately 600 times. This system has also been used to record the effect of anharmonically produced phonons in GaAs [Mahler, et al., 1963] and in $NaClO_3$ [Mahler and Tanttila, 1963].

The boxcar integrator zero point may be shifted and the gain increased to obtain a full scale recording of a much smaller effect. The limit of the effect which may be observed is determined by the stability of the equipment, the signal-to-noise ratio, and the learning time constant. Under noisy conditions or conditions where only a small effect is observed, the integration constant is made several times longer than the sampling pulse to obtain a less noisy trace. The sweep time must be correspondingly increased to allow the integrator time to follow the desired variation in signal height. The effective time constant which may be used to determine the necessary sweep time is obtained by dividing the product of the learning time constant and the time between samples by the length of the sampling pulse. The sweep time should be greater than 100 times this effective time constant in order to obtain a smooth recording. To avoid waiting for the capacitor to charge to the correct voltage at the start of a recording, the capacitor voltage may be set by using the output-voltage-set provision.

One of the main advantages of this system in practice has proven to be the ability to obtain a recording of an effect too small to be seen with previous equipment. A recording of an absorption curve

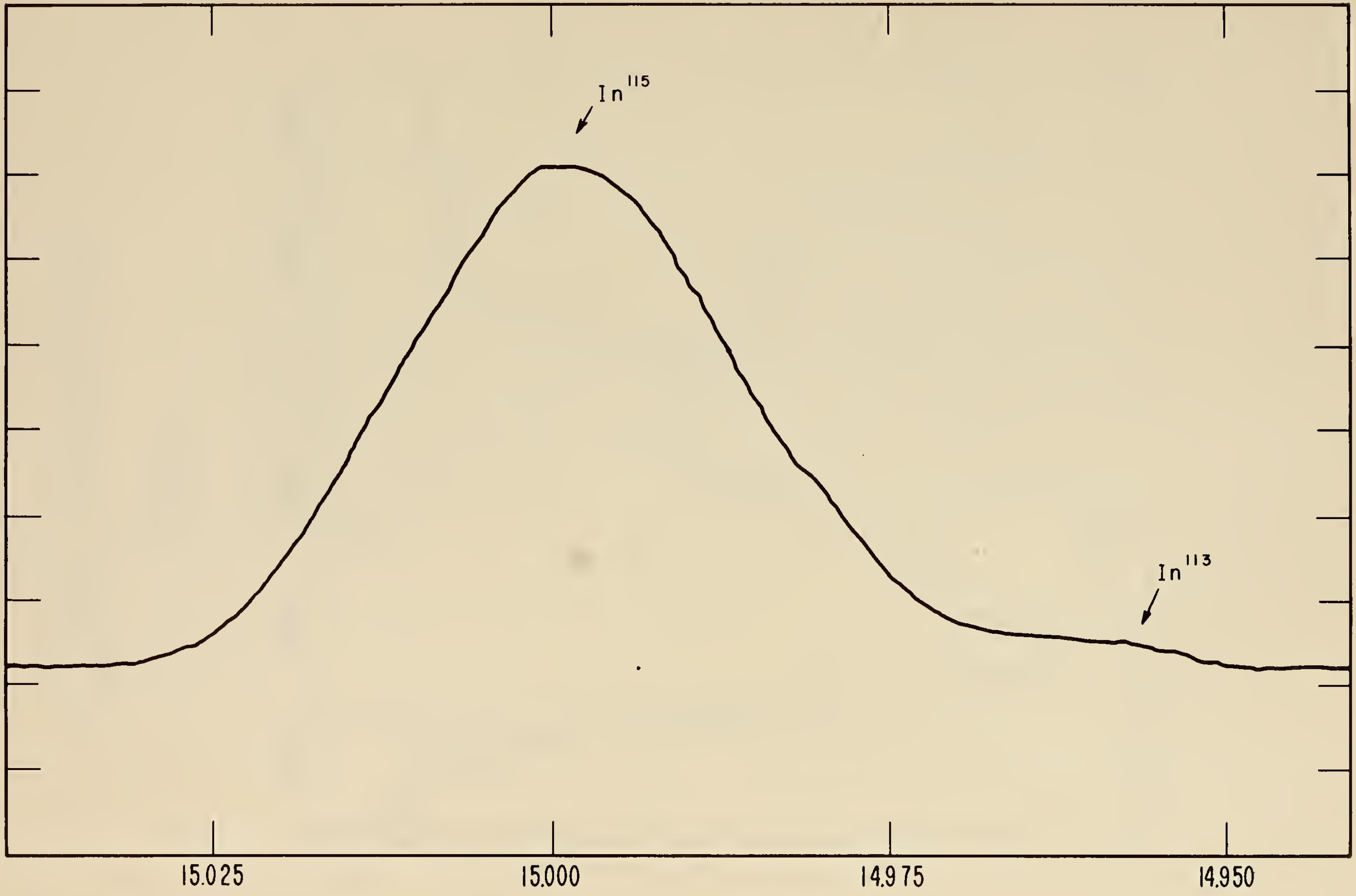


Figure 4

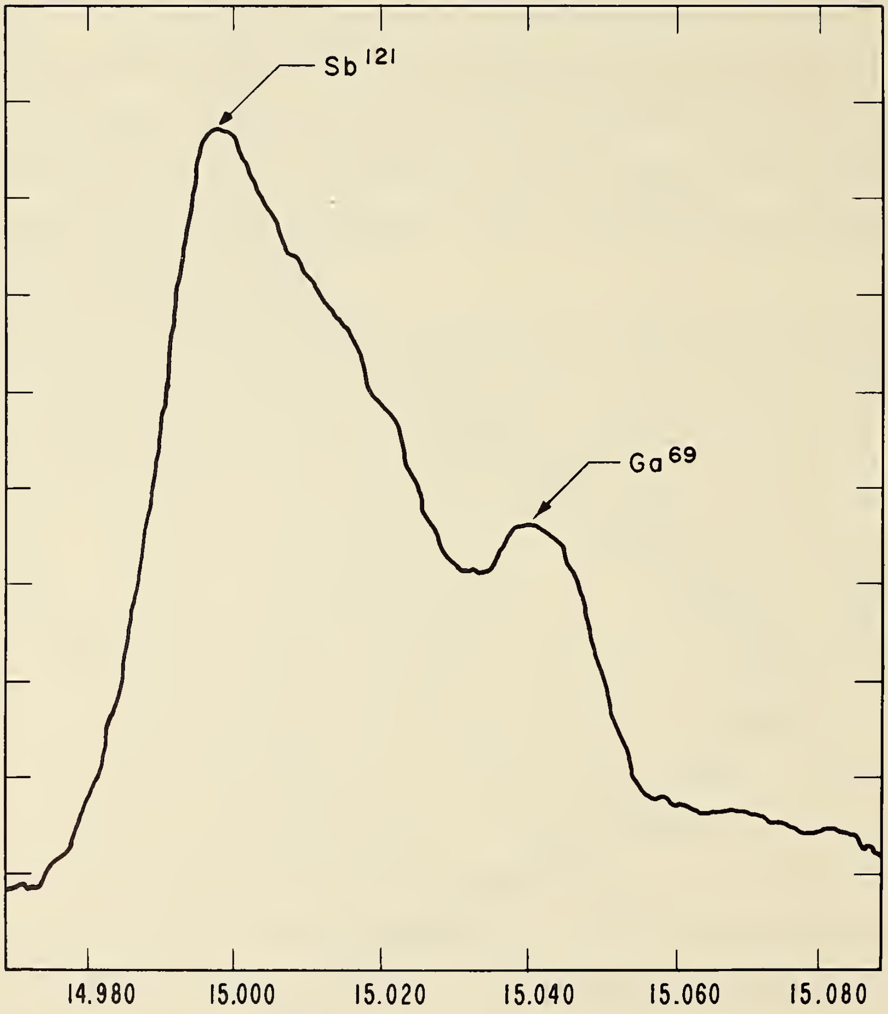


Figure 5

Sb^{121} and Ga^{69} Resonances in GaSb

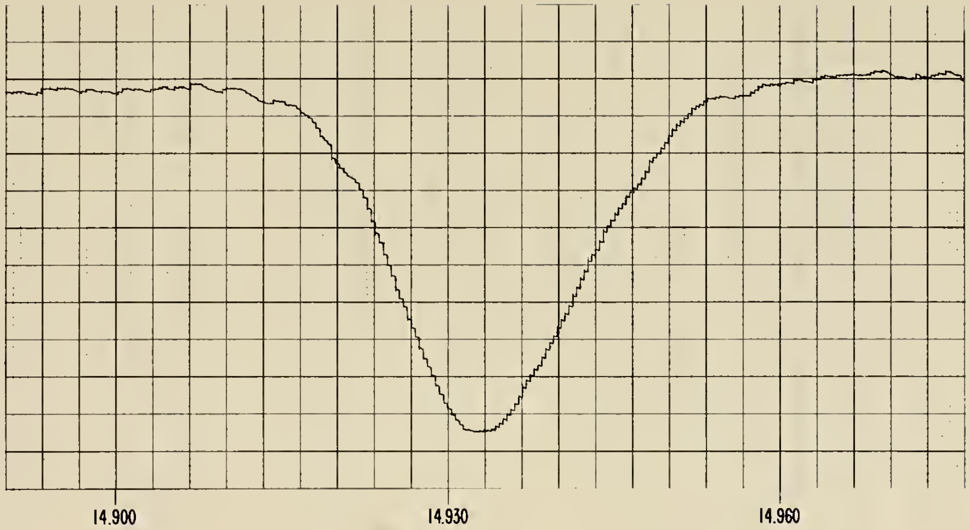


Figure 6

Hexadecapole Interaction In^{115} Resonance in InAs representing a 2 per cent reduction in height of the NMR signal is shown in Fig. 6. This figure shows the first experimental evidence of the hexadecapole interaction [Mahler, et al., 1966]. The NMR system was at 5 MHz and the ultrasonic energy at 15 MHz to induce $\Delta m = \pm 3$ transitions.

4. Acknowledgements

The author is indebted to Dr. W. H. Tanttila for proposing the principle of operation used, and to Dr. R. J. Mahler for the original ultrasonic absorption work with the InSb and GaSb crystals.

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