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Locked Nuclear Quadrupole Resonance Spectrometer for Pressure Measurements

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The Nuclear Quadrupole Resonance frequency of a nucleus in a solid is dependent on its local environment and can be quite sensitive to changes in temperature and pressure. A spectrometer capable of locking accurately to the center of a resonance signal is described. The feasibility of using the quadrupole resonance frequency as a transfer gage for precise pressure measurements is discussed using ^{35}Cl resonance in a $KClO_3$ polycrystalline sample. The performance of the instrument implies a limiting accuracy for pressure measurements of 0.7 bar; preliminary results are presented showing frequency versus pressure curves near room temperature. Uncertainties of these measurements are primarily due to inadequate temperature control and the uncertainty of the pressure measurement.

Key words: $KClO_3$ nuclear quadrupole resonance; pressure transducer; spectrometer.

1. Introduction

Many workers in the field of nuclear quadrupole resonance (NQR) have for some time been interested in the temperature and pressure dependence of the NQR frequency. The first theoretical treatment was given by Bayer [1][1] who considered temperature effects in terms of molecular vibrations. Kushida, Benedek, and Bloembergen [2] expanded the theory to take into effect thermal expansion and compressibility. Their results suggest that the NQR frequency might be useful as a sensing device for temperature, and in principle it could also be used to measure pressure. A material suitable for such experiments should be characterized by a strong resonance signal, a relatively narrow line width, and a lack of hysteresis. One such material, which has been considered for an NQR thermometer [2–6], is $KClO_3$. In the early experiments, NQR spectrometers were not locked to the center of the resonance line and the experimental accuracy was of the order of 0.002 K. Volpicelli et al. [7] have described a system for locking the spectrometer to the center of the resonance line. Most recently Utton [8] using a spectrometer locked to the center of the resonance line has been able to measure the temperature in the range 50 to 297 K to an accuracy of ±0.001 K.

The effects of pressure on the ^{35}Cl NQR frequency in $KClO_3$ [2,2a] are not as great as the temperature variations, i.e., $\left(\frac{\partial f}{\partial T}\right)_P \simeq 5$ KHz/°C at room temperature while $\left(\frac{\partial f}{\partial P}\right)_T \simeq 30$ Hz/bar.[2] Nevertheless, we decided to examine the feasibility of using the pressure dependence of the quadrupole resonance frequency as a method to measure pressure with high precision. If it could be shown that the resonance frequency is a stable, single-valued function of both temperature and pressure, and that its dependence on contamination and crystallinity and other sources of error is below a certain value, then the quadrupole gauge would have one great advantage over other types of transfer gages: once the pressure-temperature dependence of the quadrupole frequency for a particular material had been established, any number of transfer gages could be reproduced and used within established limits of uncertainty without further need for calibration. In contrast all of the transfer gages presently available require initial calibration and frequent recalibration depending on their use.

It is clear from the nature of the application for which this spectrometer was designed, that it must be very stable; in addition, the sensitivity characteristics must be good because of the small sample size dictated by the geometry of the pressure vessel. This paper describes an improved version of the NQR tracking spectrometer used by Utton [8] for temperature studies.

With this system we have been able to track the ^{35}Cl NQR signal in $KClO_3$ and measure the center frequency of the ^{35}Cl resonance to 1 percent of the line width [3] for pressures up to 2 kbar. In constructing a calibration curve

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[1] Figures in brackets indicate the literature references at the end of this paper.

[2] 1 bar=10^5 N/m^2.

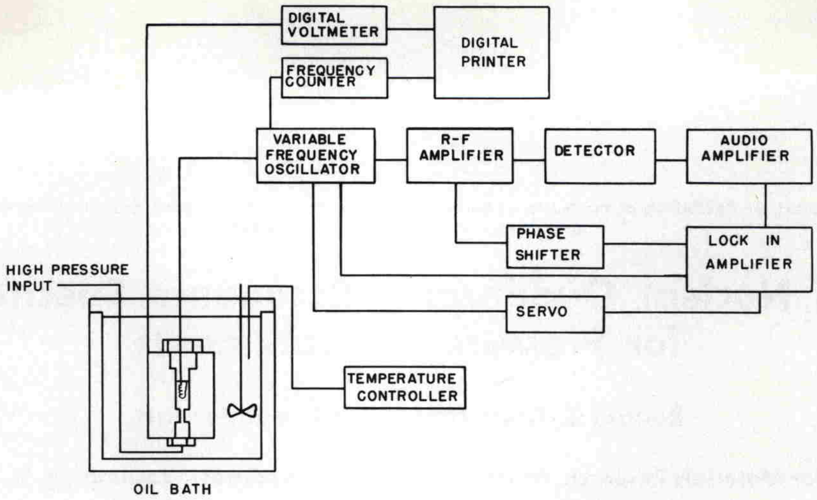

FIGURE 1. *Block diagram of NQR Spectrometer.*

the best pressure uncertainty in the range 0–2 kbar, is at present 0.15 bars at 2 kbars and the percent error is about the same over the range [9]. The fluctuation in the temperature is reflected in the uncertainty of the frequency measurement at each pressure point and would correspond, based on the known temperature coefficient of $KClO_3$, to about 0.25 bars when the sample temperature is held constant to ± 0.001 °C. The uncertainty in the frequency counter is ± 1.0 Hz. or about 0.03 bars. Hence the limiting uncertainty for determining the pressure from a frequency measurement, using such a calibration curve, would be about 0.7 bars.

2. Instrumentation

2.1. Oscillator

A block diagram of the quadrupole spectrometer which was used for the high pressure NQR studies is shown in figure 1. The oscillator detector circuit is given in figure 2. The oscillator detector circuit is a modified version of the circuit described by Pound and Knight [10] and is essentially that used by Utton [8]. The oscillator is of the marginal type and oscillation is maintained by a nonlinear negative resistance provided by the tube feedback circuit [11]. The variable capacitors C_1, C_2 are used for coarse and fine tuning of the oscillator, and the voltage variable capacity diodes (VCD) are used for frequency tracking and frequency modulation. VCD1 can also be used for tuning and will be discussed later. For various applications different values of L can be used to obtain any desired operating frequency. The r-f level at the sample coil can be varied by adjusting the gain control, Rg, or by adjusting the feedback. At 28 MHz, for example, the r-f level is adjustable over the range 0.02–2.20 V.

2.2 R-F Amplifier

The oscillator is followed by a three-stage stagger tuned r-f amplifier. By tuning each stage of an amplifier at slightly different frequencies it is possible to achieve a gain bandwidth product greater than that of synchronously tuned cascade stages. The selectivity curve can also be tailored to fit a prescribed response such as a flat band pass with very good gain [12]. The choice of a flat band pass r-f amplifier is suggested by the operation of the oscillator detector circuit [10]. In the oscillator the level of oscillation is sensitive to the shunt impedance across the tank circuit. As the frequency is varied the corresponding change in the shunt impedance results in a change in the r-f level. This undesirable change in level is compensated for by feeding back part of the r-f rectified voltage in such a way as to control the value of the negative resistance, thereby holding the level of oscillation constant at a level far below natural limiting. In the case where the frequency of oscillation is expected to vary over a large range, as in a tracking spectrometer, it is desirable to have the voltage gain of the r-f amplifier constant over the frequency range of operation. As a result the d-c feedback voltage, which controls the r-f level, is returned to the oscillator essentially independent of frequency within the band pass. The time constant for this feedback loop, of course, is long compared to the modulation frequency, which contains the signal information.

The r-f amplifier used in this spectrometer was designed, using the prescription of Valley and Wallman [12], for a center frequency of 28 MHz and 6 MHz bandpass.

Knowing the bandwidth of each stage and the central frequency one can easily calculate the circuit component values. In figure 3 the a-c equivalent circuit of a typical stage is shown. Given the stage bandwidth, B_i, the loading resistor R_i can be calculated from the relation $B_i = (2\pi R_i C_i)^{-1}$. The capacity C_i is the sum of the output capacity of T_i plus the input capacity of T_{i+1} plus wiring capacity; and the tuning coil, L_i, is wound to resonate with C_i at the appropriate center frequency. An oscilloscope trace of the band pass for this amplifier is shown in figure 4.

In a cascaded linear amplifier without feedback the

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[3] Distance between first derivative extrema.