

## AN IMPROVED CW NMR BROAD-LINE SPECTROMETER FOR WEAK SIGNAL DETECTION

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### SUMMARY

*In the article there is described a frequency-sweep nuclear magnetic resonance (NMR) spectrometer when a static magnetic field runs at a fixed value. The repetitive frequency-sweep of oscillator is realized by a variable frequency divider in the feedback loop of the second-order Phase Locked Loop. The largest advantage of this system for the CW NMR spectrometer is a good possibility of repetitive passages over resonance in case when NMR signal is very weak and the S/N ratio increase is necessary. The experimental results show that this system with the low-noise NMR oscillator is very useful for the detection of the broad-line NMR signals.*

**Keywords:** cw NMR spectra, low noise oscillator, PLL, NMR spectrometer, cw NMR broad-line spectroscopy

### 1. INTRODUCTION

The nuclear magnetic resonance is a widely used method applied in investigating molecular structure of solid state. The broad-line NMR measurements are useful tool for a study of the detailed structure of solid polymers and plastics, since fluctuations of the molecular mobility are directly reflected in the changes of the NMR spectrum. The broad-line NMR spectra can often be decomposed into elementary components reflecting different kind of mobility of the matter structure, e.g. macromolecular chains in a polymer [6]. For this reason a *distortionless line shape* record is necessary.

By this method, the absorption of energy from a radio frequency (rf) field by a nuclear spin system is detected. The resonance occurs at the angular frequency  $\vec{\omega}$  given by

$$\vec{\omega} = \gamma \vec{B}, \quad (1)$$

where  $\vec{B}$  is the induction of the static magnetic field,  $\gamma$  is the gyromagnetic ratio of the nuclear characteristic of the particular spin system. For protons 1mG corresponds to 4.25776 Hz. In most of the NMR experimental systems a marginal rf oscillator is used to produce the rf field. The NMR spectrometer described in this paper has been used with a JFETS based *autodyne oscillating detector of the Pound-Knight-Watkins type* which can be operated at rf levels down to 0.5 mV. Most of the oscillator of this type that are described in literature are not tunable, while the frequency-sweep NMR spectrometer described in this paper is tunable over a kilocycle frequency region by the PLL (phase locked loop) method.

### 2. DESCRIPTION AND OPERATION OF THE SPECTROMETER

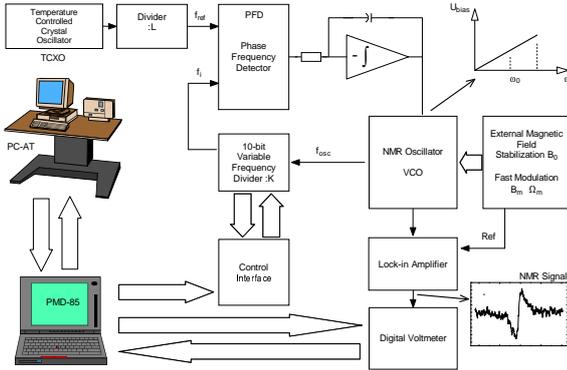
The NMR absorption line in a differential form is detected by a repetitive oscillator frequency sweep and it requires the static magnetic field to be run at

a fixed value in the duration of the multiple pass experiment, i.e. for a period of several days, because the signal-to-noise ratio is quite small and signal averaging is necessary. Also the oscillation level has to remain constant during the sweeps and large sweep amplitudes may be employed even at low oscillation levels. Since the spin-lattice relaxation times in most solids are very long, the low levels of rf excitation must be maintained for the NMR in order to avoid saturation of the specimen while sweeping through the resonance region. The shape of a resonance line can be disturbed due to the instabilities of both: the frequency and amplitude of the rf field. We have used a new solution in constructing the CW NMR measuring apparatus, by involving the using of the computer controlled PLL frequency-sweep NMR oscillator. The oscillator circuit of the spectrometer is considerably *less sensitive* to unwanted  $\chi'$  nuclear susceptibility component even in case of a very small signal-to-noise ratio, when the signals averaging is necessary.

The above experimental situation essentially requires a step by step frequency controlled autodyne NMR circuit. Using PLL techniques we have achieved a typical performance of frequency stability within one-part in  $10^8$  over several hours between the frequency steps controlled via personal computer.

In figure 1, we can see that the frequency of the NMR oscillator is led to the variable divider (10-bit resolution) which provides the required division derived from the own output frequency of this variable divider. There is the control interface either to synchronize the measuring between a PC and a digital voltmeter or to realise reset control. Using this block we can change the speed of sweeping automatically or manually as well. On the other hand, the output frequency from the variable divider is transmitted to one of the inputs of the phase-frequency detector (PFD). To another input of the same circuit (PFD), which creates the responsible output voltage, we have connected the reference frequency from the temperature controlled crystal oscillator (TCXO) predivided by factor  $L$  defining the bandwidth of the sweep. The

oscillator frequency step will be  $\Delta f/1023$ . In a state, when PLL is in lock, the frequency must be (see figure 1)



**Fig. 1** Block diagram of the spectrometer

$$f_i = \frac{f_{osc}}{K} = \frac{\Delta f}{1023}, \quad (2)$$

where  $\Delta f$  is a sweep bandwidth,  $K = N + 13312$ ,  $N$  is a divide factor of the variable 10-bit divider, and 13312 is a preset divide number [8].

For a central oscillator frequency  $N = 512$  and  $K = 13824$  the (2) is rewritten to

$$f_{osc} = \frac{\Delta f}{1023} \cdot K. \quad (3)$$

We can write the absorption line bandwidth in the units of the magnetic induction (i.e. in NMR it is G-

gauss). Then the sweep range  $\Delta B$  is given by

$$\Delta B = \frac{1023}{K \cdot 4.25776 \cdot 10^{-3}} \cdot f_{osc}, \quad (4)$$

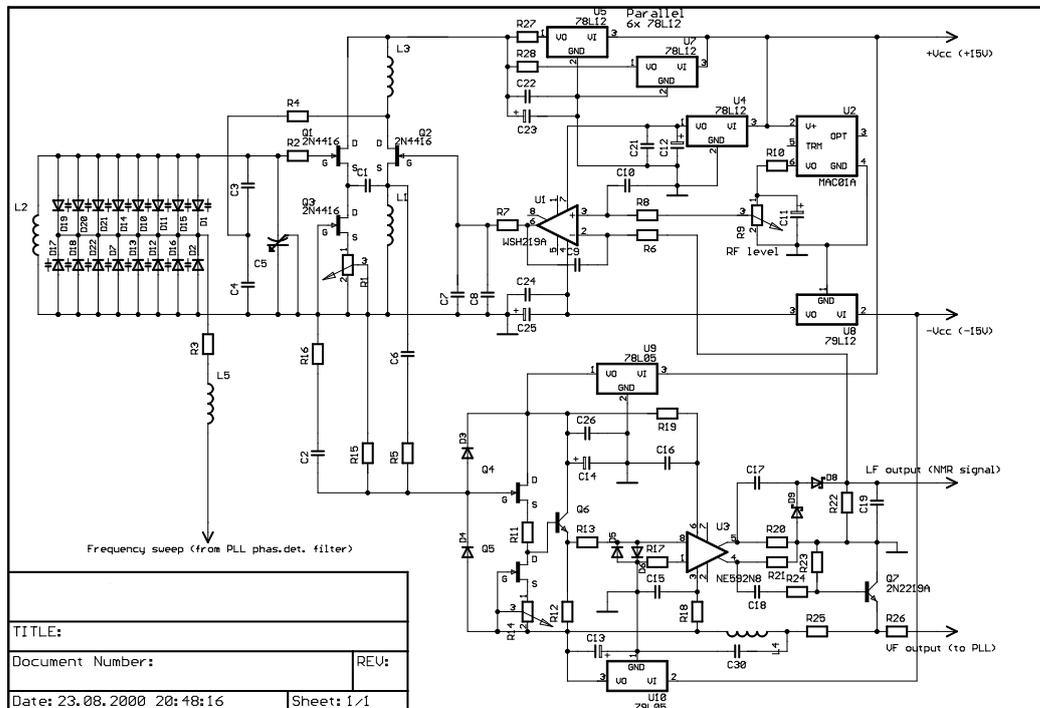
where  $f_{osc}$  is substituted in Hz.

The circuit, shown in figure 2, comprises three stages:

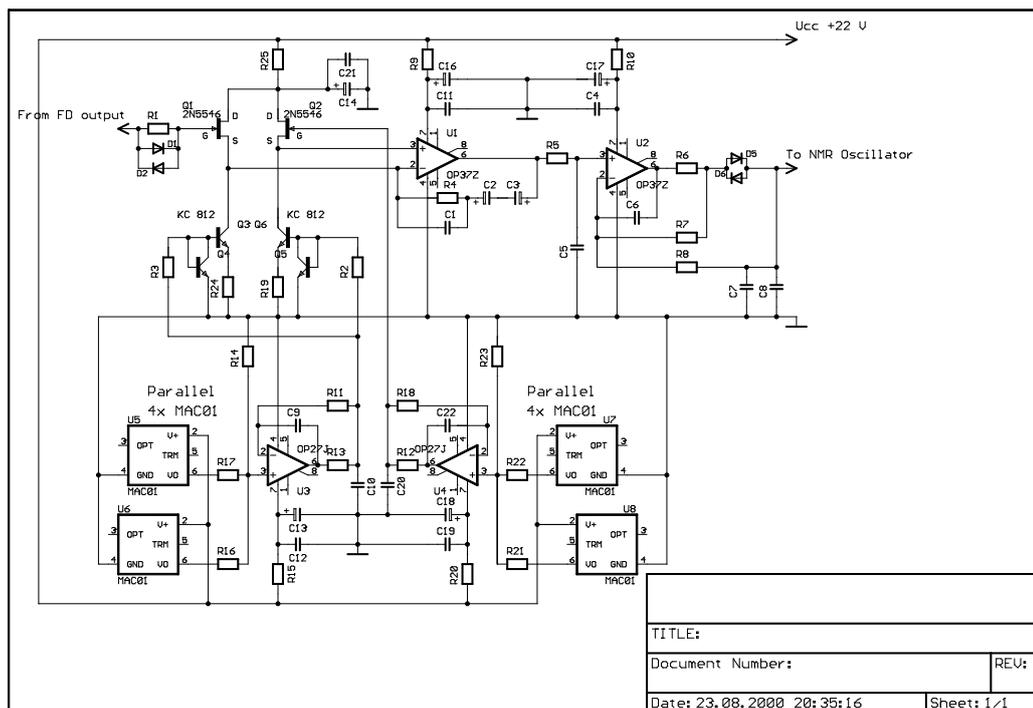
1. a rf level limited oscillator,
2. a high frequency feedback amplifier and detector and
3. a low-noise integrator for the automatic rf level control.

In the oscillator part of the autodyne oscillating detector we have employed two low-noise JFET transistors 2N4416 from Texas Instruments, heaving a low-noise figure, high gain and provide wide bandwidth. As a high frequency amplifier, there is applied a simple monolithic integrated circuit of a type NE 592. From the symmetrica outputs of this circuit we obtain a large amplitude of rf voltage both, for a simple diode detector and for a feedback to stabilize the amplitude of oscillations.

After appropriate frequency division the frequency of the NMR autodyne oscillating detector circuit is compared with the 5 MHz reference frequency divided according to our needs via TCXO. The output voltage from the phase-frequency detector is amplified via the integrated circuit integrator and the filter (see figure 3) which provides the bias voltage for the NMR tank circuit varactor diodes (see figure 2).



**Fig. 2** Schematic circuit of the low-noise NMR oscillator. The six parallel-output connected voltage regulators 78L12 reduced the relative noise at the output of the supply voltage. MAC01 is a +10V precision voltage reference (REF01). The Q1–Q5 are high-performance high-frequency n-channel JFET transistors. The WSH 219A is a low noise hybrid JFET op-amp for differential integrator for the automatic rf level control. The R9 is a 10-turn pot adjusted to select the required rf level. The R1 is adjusted to get a signal having the best ( $\frac{S}{N}$ ) ratio. Multiple tuning diodes are used to reduce the circuit's phase noise. The circuit has been operated at rf levels ranging from 500 mV down to 0.5 mV



**Fig. 3** Schematic circuit of the phase-frequency detector filter. The 2N5546 is the low-noise matched pairs of JFETs. The KC812 is the matched pairs npn and the op-amp U2 performs the fast setting low-pass filter

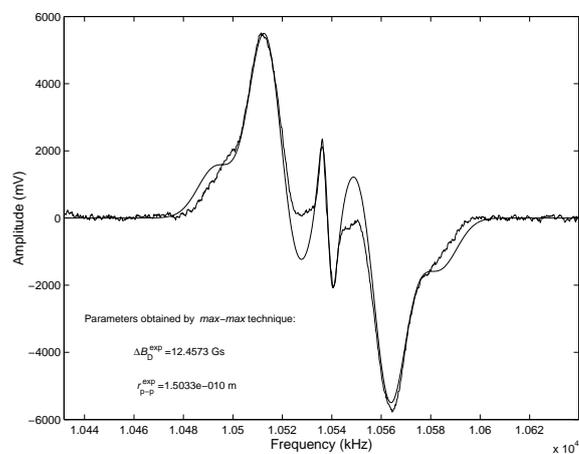
The NMR signal in the digital form is recorded into the personal computer memory (or via a printer) and via the computer the frequency steps of the NMR oscillator sweep are controlled as well. This solution of the slow modulation of the CW NMR spectrometer guarantees an exact agreement between the computer memory addresses and the NMR frequencies.

Data acquisition and processing are realised by a system consisted of an acquisition computer and a host computer. The acquisition subsystem is a complete 8-bit computer linked to the host 32-bit computer via parallel interface (see figure 1). The host computer performs the functions of data acquisition, storage, data analysis and communication. The acquisition computer provides the averaging of the NMR signal and processing control. Using this architecture system we have expanded the capabilities of our NMR spectrometer.

### 3. RESULTS

The described spectrometer was tested by recording weak NMR signals, especially from solids, at room temperature. The presented signals were recorded by linear averaging. We tested the ability of spectrometer experimentally by measuring the proton distance in water molecule from the splitting of the NMR line of a pair of protons in the monohydrate  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  powdered samples (gypsum). The splitting was discovered by Pake [7] and was also measured by other techniques (e.g. pulsed NMR, neutron diffraction). Its value is 0.158 nm [1, 4, 5]. Notice, that the line width  $\Delta\omega_D$  is related to the internuclear distance  $r$  as  $\Delta\omega_D = 3\gamma^2\hbar\mu_0/8\pi r^3$  and can be obtained experimentally with a fairly good precision

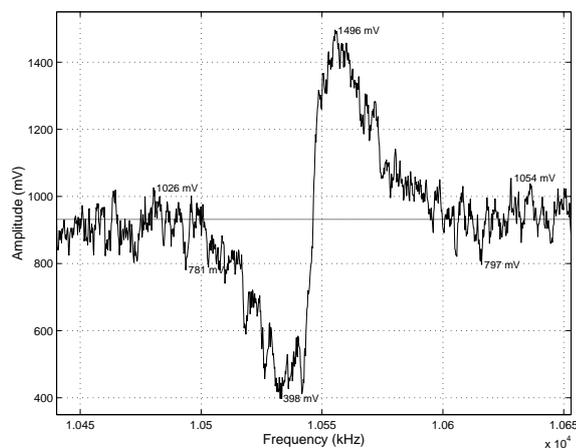
from the maximum value of the line spacing of the differentiated NMR absorption spectra (max-max technique see figure 4).



**Fig. 4** Differentiated NMR absorption spectra of crystallization water in polycrystalline monohydrate  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  after averaging and computed simulation of spectra with parameters acquirment optimizing program worked-out by Hronský et al. [2]. The experimental spectrum was recorded by the storage of 16 spectra from about 2 g of pressed powder sample at the amplitude of modulation 0.46 G and working frequency 10538 kHz. The filling factor was 0.07 and temperature of sample 300 K, respectively. The rf amplitude peak-to-peak  $2B_1$  was set to the value 0.09 mG to avoid saturation, which corresponds to the amplitude of the rf voltage  $U_{pp}$  on the coil with the sample 1.8 mV. The smoothed curve shows the best-fit computing simulation spectra. The calculated points fitted to the gypsum curve (smoothed) have  $2\alpha = 10.7$  G, from which the p-p distance is 0.158 nm

In figure 4 the classical “Pake doublet” is broadened by homonuclear dipolar interactions. The calculated points fitted by the optimizing program worked-out by Hronský et al. [2] to the gypsum curve (smoothed) have  $2\alpha = 10.7\text{G}$  for which the p-p distance is 0.158 nm. The recordings of the signals were entirely satisfactory.

In figure 5, we demonstrate the sensitivity and stability of our equipment for the weak signal record detected for one hour. The long term drift in the frequency and magnetic field was measured with repetitive records of the NMR signals from poly(methyl methacrylate) samples (figure 5). The total instability in the recorded spectra during 57 hours was less than 20 ppm at the resonance frequency 10.545 MHz, it means about 1% for the 0.5 mT (5 G) NMR linewidth.



**Fig. 5** Spectrum from poly(methyl methacrylate) sample volume  $125\text{ mm}^3$  (about 0.2 mg) at temperature 300 K. The amplitude of modulation was 0.46 G and frequency of modulation 39.5 Hz. The sweep rate of the recording 14 mG/s and rf amplitude  $2B_1$  peak-to-peak was 0.22 mG, filling factor of the sample was 0.009 (volume of the sample is approximately is a 1/59 fraction of the rf coil volume).  $\left(\frac{S}{N}\right)_{pp}$  calculated according to Hull is approximately equal 10 [3]

#### 4. CONCLUSION

The computer controlled PLL frequency-sweep techniques, which is used with our low-noise NMR oscillator, gives a much improved performance compared with conventional CW NMR detector circuits. The simple nature of the presented low-noise NMR oscillator and phase-frequency detector filter enables a compact printed circuit layout with necessitating complex interstage shielding without any critical layout of components. The enhanced sensitivity of the

low-noise NMR oscillator allows it to operate at low rf fields and the overall simplicity of the circuit makes it an excellent CW NMR detector, especially useful for probing weak signals at wide temperature range for their distortionless line shape record.

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#### BIOGRAPHY

**Ladislav Ševčovič** was born in Leles, in 1952. He is graduated in Experimental Physics of Solid State from the Comenius University in Bratislava, in 1976. He received the Dr degree in 1985 in the field of Physics of Solids at the Pavol Jozef Šafárik University in Košice. His professional area concerns the Nuclear Magnetic Resonance phenomena in Solid State and his scientific research is focusing on the experimental equipment of NMR. In addition, he also investigate problems related to dynamic properties of polymers by NMR methods.