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REVIEW OF THE STRUCTURE AND THE PRINCIPLE OF WORK OF NUCLEAR QUADRUPOLE RESONANCE THERMOMETER

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ABSTRACT

Nuclear quadrupole resonance which was first described in Dehmelt and Krüger's articles in the middle of XX centuries, formed the basis of the nuclear quadrupole resonance thermometer. The essence of the phenomenon of nuclear quadrupole resonance is that, if a substance is placed in an electromagnetic field with a frequency equal to the frequency of the quantum transition of electrons to another energy level in the nuclei of the substance, it will be observed energy absorption of this electromagnetic field. Since it is known that the frequency of the quantum transition between energy levels is a function of temperature of environment in which a substance take place, that has characteristics of nuclear quadrupole resonance, then this effect can be used to measure temperature. In article present the history of development and the structure, and principle of work of nuclear quadrupole resonance thermometer.

Index Terms - quadrupole moment, quadrupole resonance, nuclear quadrupole resonance thermometer, isotope, spin number, resonance circuit, spin number.

1. INTRODUCTION

Temperature measurement has always been one of the most common questions regarding the measurement of physical quantities. Temperature measurements are present in almost any experiment, and play a key role. Temperature, unlike other physical quantities cannot be measured directly. The temperature change can be traced by the change of other physical properties of probe (volume, pressure, electrical resistance, radiation intensity, etc.) related to the temperature of certain laws. But all these properties are not allowed to achieve such precision temperature measurement as a method for measuring the nuclear quadrupole resonance (NQR) effect, which occurs at the atomic and molecular level, and allows the realization of a thermometer with measurement accuracy of 0,001 K.

The main goal of this paper is divided into two main parts. The first is about the history of studies of effects that were the basis for the creation of nuclear quadrupole resonance thermometer, and the second is description of the structure and principle of work of this thermometer.

2. HISTORY OF STUDIES

2.1 Nuclear quadrupole moment

In the spring of 1935, T. Schmidt and H. Schüler reported that the distance between the certain hyperfine lines in the atomic spectrum of the two europium isotopes ^{151}Eu and ^{153}Eu did not follow, generally accepted at that time, the Lande interval rules. The reason of that phenomenon is that the nuclei of these isotopes have deviation from spherical symmetry η [1]. Just out of it comes the concept of the nuclear quadrupole moment Q, usually expressed in units of 10^{-24} cm^2 = 1 barn. Nuclear quadrupole moment is some quantity that characterizes the deviation from the spherical shape of the nucleus [2]. It is important to know that the shape of the nucleus is closely connected with distribution of nuclear charge, or in other words, gradient of the electric field. Components of the electric field gradient are

$$q_{xx} = \frac{\partial E_x}{\partial x},\ q_{yy} = \frac{\partial E_y}{\partial y},\ q_{zz} = \frac{\partial E_z}{\partial z}. \ (1)$$

When all three values are different, by convention, q_{zz} refers to the largest field gradient, q_{yy} the next largest, and q_{xx} the smallest. When all three components of the field gradient are the same - the field gradient is spherical, and all the quadrupole levels, which are briefly discussed below, are degenerate. When $q_{zz} \neq q_{yy} = q_{xx}$ there is axial symmetry around the z axis [3].

Deviation from spherical symmetry along the principal z axis, or asymmetry parameter of the field gradient can be presented as

$$\eta = \frac{q_{xx}-q_{yy}}{q_{zz}}. \ (2)$$

In all cases

$$0 \leq |\eta| \leq 1. \ (3)$$

It also can be said that electrical quadrupole of nucleus interacts with his surrounding electrons [4]. These two phenomena are closely related to each other. By the way, in a later paper, the word "quadrupole" was given by the two above mentioned authors, following a suggestion by Delbrück [5,6].

Nuclear quadrupole moment arise only when a nucleus has a spin $I > \frac{1}{2}$; nucleus with spin 0 and $\frac{1}{2}$ is spherical. A large number of nuclei of the periodic system have a quadrupole moment [7]. Prolate nucleus along the direction of spin has positive and oblate - negative quadrupole moment. Normally the scalar quadrupole moment is usually determined as

$$eQ = \langle \sigma(3z^2 - r^2) \rangle_{avg}, \ (4)$$

where σ - nuclear charge density as a function of position, z and r - coordinates of charge element, e - the magnitude of the charge on an electron.

The spherical, nonspinning nucleus in Figure la is a representation of nuclei where I and eQ are zero. Figure 1b, as figure 1a, represents spherical charge distribution, that's why eQ = 0, but spin number is equal $\frac{1}{2}$. In figures 1c and 1d, net spin of all nucleus particles is equal or greater than 1 and nuclear quadrupole moment $Q \neq 0$, but the sign of Q allow to determine is nucleus oriented along the direction of the applied field vector or perpendicular to the principal axis. Statement that, nucleus on figure 1a possesses a lower energy state than on figure 1b is also true, and it can be also treated as energy levels. [7].

Transitions between adjacent energy levels can be initiated by electromagnetic radiation of frequency ν, provided the Bohr condition $\Delta E = h\nu$ [8].

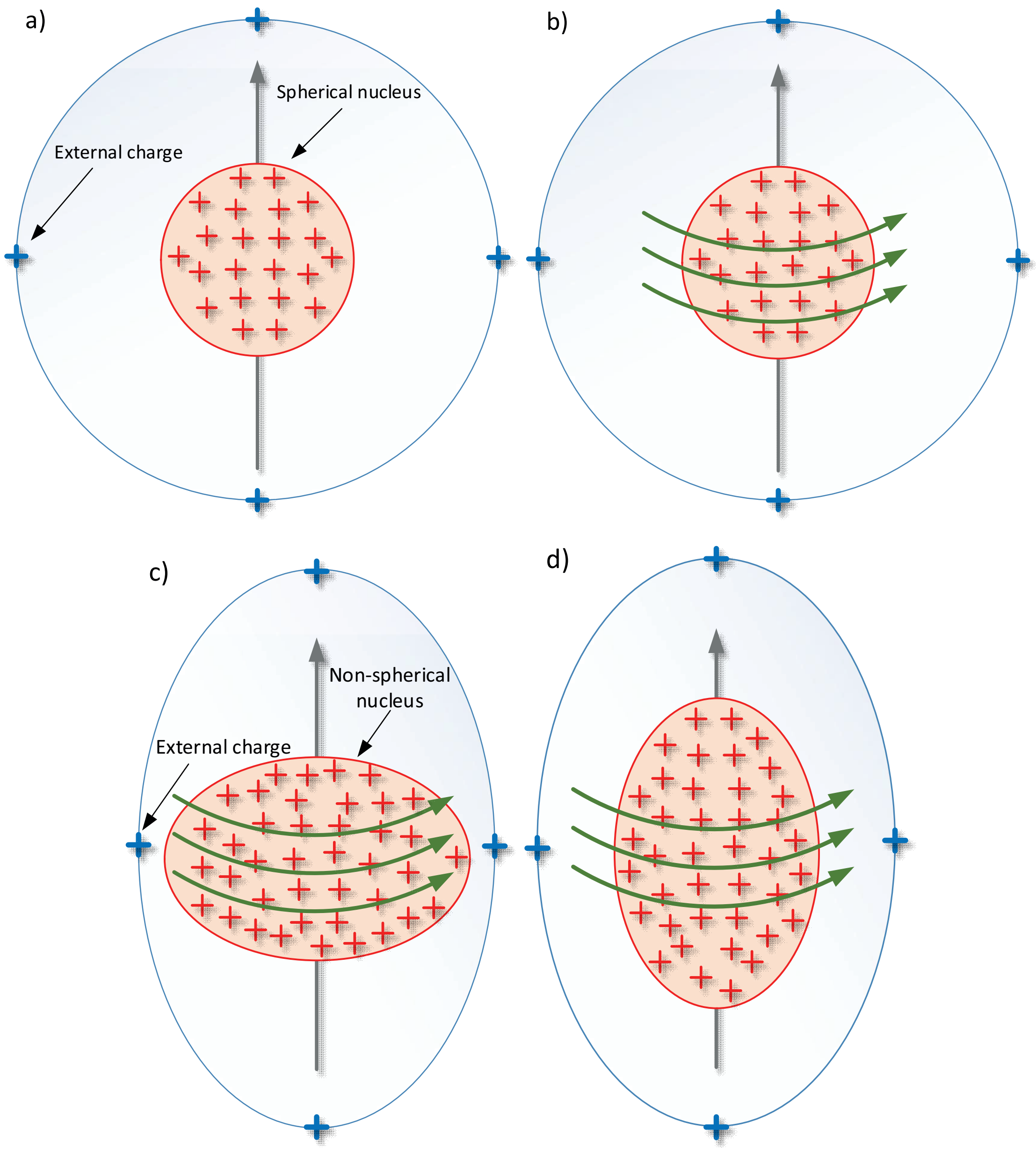

Figure 1. Representation of nuclei for a) $I = 0$, $eQ = 0$; b) $I = \frac{1}{2}$, $eQ = 0$; c) $I \geq 1$, $eQ < 0$; d) $I \geq 1$, $eQ > 0$;

2.2 Nuclear quadrupole resonance

As already mentioned, in crystals, under the influence of the interaction of nuclear quadrupole with the electric field of molecules electron shells, or more precisely, the electric-field gradient, occurs orientation of nuclear spins in a certain direction. If perpendicular to this direction apply radiofrequency field, whose frequency is equal to the frequency of transition between levels, the absorption of radiofrequency power can be observed. This phenomenon was first discovered by german scientists H.G. Dehmelt and H. Krüger in 1950 [9]. In this and the following paper [10], the authors investigated the resonant radiofrequency absorption resulting from transitions between levels of the nuclear electric quadrupole splitting in Cl and Br nuclei. According to the formula $\nu = \frac{|eQq_{zz}|}{2h}$ was calculated frequencies for isotopes ^{35}Cl, ^{37}Cl, ^{79}Br, ^{81}Br, which all have spin $I = \frac{3}{2}$. Also, it should be noted the unsuccessful attempt of

Pound [11], who, because of wrong choice of research object, has been forced to admit bad result at about the same time as the Dehmelt and Krüger.

NQR is used to obtain detailed information about the crystal symmetry and bonds of the crystal lattice, structure changes with pressure and temperature and at phase transitions in solids, determination of quadrupole moments of nuclei, the nonequivalence position of resonating nuclei in the crystal grid, moments of inertia of the molecular groups, research of types and degree of hybridization of covalent connections. NQR is also used for search and identification of drugs and explosives, remote luggage control.

2.3 Dependence of the quadrupole resonance frequency on pressure and temperature

Quadrupole resonance frequency is a function of thermodynamic state of the body under investigation. One year after the discovery of NQR, the theory of the dependence of this phenomenon on the temperature has been developed by Horst Bayer [12], which took into consideration rotational vibrations of nuclei, leading to averaging the electric field gradient. This theory was experimentally confirmed in Dean and Pound's article where they investigated the resonant absorption in several solid benzene compounds [13]. Also, the theory was discussed in more detail in other studies, where other lattice vibrations were taken into account [4, 14]. According to this theory, the average internal field gradient at the nucleus decreases with increasing temperature solely because of the increase in the amplitude of the thermal vibrations [14]. Almost all experiments show that a temperature increase decreases the NQR frequency.

The most detailed analysis of the frequency dependence on temperature and pressure was described by the Harvard University's scientists [14]. General relation between frequency ν and temperature T and additional formulas are presented.

$$\nu = \nu_0 \left[1 - \frac{3}{2} \sum_{i=1}^{N} \frac{A_i}{\omega_i^2} \hbar\omega_i \left(\frac{1}{2} + \frac{1}{e^{\left(\frac{\hbar\omega_i}{kT}\right)} - 1} \right) \right], (5)$$

where ω_i is the eigenfrequency of the ith mode of vibration and

$$\nu_0 = \frac{eQq_0 \frac{3}{2}(2m_z - 1)}{2I(2I-1)}. (6)$$

ν_0 is a frequency at 0 °K in absence of zero point energy.

Here A_i - an inertia factor which is in $kg^{-1}m^{-2}$ units, is defined by $A_i = a_i - \frac{2}{3}\delta_{i\,i}$, where a_i and $\delta_{i\,i}$ are coefficients in the following expansion:

$$\theta = \sum_i a_i \xi_i + \cdots, (7)$$

$$q = q_0 \left(1 + \sum_i \beta_i \xi_i + \sum_{i\,j} \delta_{i\,j} \xi_i \xi_j + \cdots \right), (8)$$

where ξ_i amplitude of the normal modes of vibration.

Pressure dependence under normal conditions often can be neglected. Measurements were carried out in the range of pressure changes from $0 kg/cm^2$ to $10000 kg/cm^2$ [14]. All measurements have shown that increasing the pressure increases the quadrupole resonance frequency.

2.4 Precise nuclear quadrupole thermometer

The first assumption that the dependence of the effect of nuclear quadrupole resonance on temperature can be used to produce an precise thermometer was made almost immediately after the discovery of the phenomenon [13]. In 1956, was first described the NQR thermometer [15]. Below is the abstract of this article: "The properties of a thermometer based upon the temperature variation of the pure quadrupole resonance frequency (ν) of the ^{35}Cl nucleus in granular $KClO_3$ have been investigated. In the range ~10°K<T <300°K, the thermometer has a very high sensitivity, being better than ±0,002° at 273°K and ±0,004° at 77°K. The accuracy at 20°K is estimated as at least ±0,02°. The thermometer is exactly reproducible if care is taken that the $KClO_3$ is of high chemical purity. No hysteresis effects were observed. Establishment of the thermometer requires a single precise determination of the ν versus temperature curve using the fundamental temperature standards to measure the temperature."

In 1965, Jacques Vanier gave a description to his thermometer [16]. The range of measurements of his thermometer was from 10K to 450K. The center frequency of the absorption line of ^{35}Cl in pure samples of $KClO_3$, at 77K was reproducible to approximately 2Hz, which correspond to accuracy better than 0,001K. The sensitivity of this thermometer was expected to ±0.0002K. But in [17] the sensitivity at room temperature is about 5kHz/°C and at liquid nitrogen temperature it is 2,5 kHz/°C; accuracy of ±0,002°C.

12K to 297K - this is studied temperature range of measurement of Utton's thermometer [18]. The combined uncertainties in the frequency and temperature measurements correspond to ±0,001K in the range 50K - 297K, deteriorating to ±0,004K at 30K and ±0,010K at 20K.

A fully automatic precision NQR thermometer has been developed [19] with reproducibility, and a stability on the order of ± 1mK at the triple point of water for a 77 to 374K temperature measurement range. Then it was calibrated at the range from 203K to 398K [20].

The same kind of thermometer was constructed in Ukraine. This thermometer can provide a measurement with accuracy of 0,001K in the range of 77-425K, and with an accuracy of 0,01K in the range of 10-77K with the sensitivity at room temperature of 5kHz/°C [21].

3. STRUCTURE AND THE PRINCIPLE OF WORK OF NUCLEAR QUADRUPOLE RESONANCE THERMOMETER

Today's NQR spectroscopy have been applied in many high-tech industries, including aviation, aerospace, and defense industries. The main advantages of NQR thermometry are:

- extremely high precision and sensitivity;
- wide measuring range;
- time stability of metrological characteristics;
- frequency output.

However, a big part of existing devices are based on analog LC-generators. This approach has several disadvantages typical for analog technology:

- time instability of fluctuations parameters;
- sensitivity to the environment influence;
- structural complexity and high levels of noise;
- the presence of nonlinear distortions caused by the use of varistors (varactors).

From the point of view of these disadvantages, it is necessary to investigate the phenomenon of NQR and design nuclear quadrupole resonance thermometer by means of modern digital technology.

The main part of NQR thermometry is oscillating circuit in which, to provide high sensitivity, will occur amplification effects of NQR. In such a circuit it will be used RLC - circuit, in which will be located a capsule with heat-sensitive material. See figure 2 below. Oscillating circuit consists of parallel-connected inductance L, capacitance C and series-connected resistors R. This is due to changes in the parameters of these elements, the resonant frequency contour coincide with the frequency of quantum transitions of nuclei of heat-sensitive substance. In practice, the role of setting frequency parameter often acts capacitance. When adjusting the parameters of the circuit, at the same time should re-tune the frequency of the excitation signal.

As already noted, in the role of heat-sensitive material (sample) is used mainly isotopes with nuclear spin values greater than $\frac{1}{2}$. In this case, as in all abovementioned thermometers, is used the potassium chlorate, which is hard-packed in hermetic and shielded shell. This capsule wrapped with coils of inductance of RLC circuit. Nuclear quadrupole resonance occurs when the signal of the resonant circuit (RLC - circuit) tuned to a frequency where there is a reduction of the amplitude fluctuations of the signal of this circuit, i.e. sample absorb the energy.

The important point for the understanding of the oscillating circuit is that it contains attenuating oscillations which should be excited by an external system. This means that if the oscillating circuit parameters, such as circuit components R, L, C are set to some of his specific values that correspond to the formation of a signal of a certain frequency, then to maintain this signal, or, in other words, to deprive the attenuation of signal, it is necessary to excite this signal with frequency, aliquot to the signal frequency. This task assumes the external system, such as system of stimulating vibrations. At present, the system described above can be realized by means of the so-called digital frequency synthesizer (direct digital synthesis, DDS), which can be extremely accurate and set probing (excitation) signal with impressive - big frequency that has critical importance to our task.

The most important part of NQR thermometer as in any measuring device is measuring channel. In this case, the measuring channel will consist of inductor, in the windings of which take place the sample, mixer and analog - digital converter.

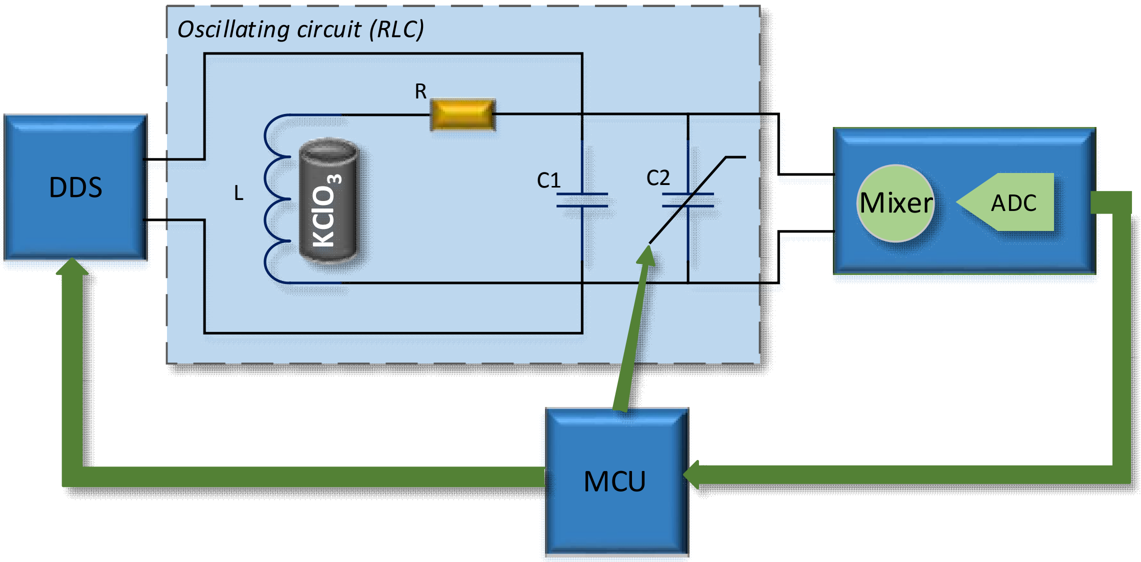

Figure 2. Structure of quadrupole resonance thermometer

In the last century, it was found that the frequency of resonance of potassium chlorate under normal conditions is ~ 28,5MHz. This, in turn, means that parameters of oscillating circuit should to be set to this frequency to detect the NQR. As mentioned above, it will be exciting signal from DDS for this circuit, which will meet the same frequency. The combination of DDS and the oscillating circuit in this case will cause the resonance of signal in oscillation circuit, i.e. on the RLC - circuit output we receive a signal with a large amplitude (resonance signal). If the resonance signal coincides with the resonance frequency of $KClO_3$, in this case, we feel the absorption of signal energy, i.e. reducing its amplitude, at the output of RLC - link.

Output DDS signal is amount units of volts, that for the detection of NQR is unacceptable to many, as the electrons of the substance ($KClO_3$) goes into saturation, which does not allow to observe NQR. The signal with the amplitude of hundreds of millivolts providing at the input of oscillating circuit, is sufficient to observe NQR. On this occasion, it's needed to put voltage divider at the entrance of RLC - circuit to reduce the amplitude of the signal from the units of volts to hundreds of millivolts. As you know the voltage divider consists of resistors, setting the values of which can change the voltage division ratio.

It is known that at resonance, amplitude of signal change in oscillation circuit is very small, up to tens of microvolts, and it plays a crucial role in determining the temperature. The ratio of the amplitude of the input signal and amplitude change of output signal is 1V/10mkV = 100000, i.e. to catch this change its needed to use high bit analog - digital converter (ADC). In this example, the ADC must have at least 17bit ($2^{17} = 131072$). Since, as noted above, the frequency modulation signal is approximately 28,5MHz, it is necessary to ensure displacement of measuring signal to low frequency areas to facilitate its further processing, especially its analog - digital conversion, as currently there are no ADC which would have a minimum of 17-bit word length and sample rate tens of MHz. The best variant for this task is to use a digital item as a mixer.

Mixer - a device for summing or subtracting the analog signals. An ideal mixer has two inputs which can receive signals of different frequencies and amplitudes, and one output from which you can get signal of their sum or difference of the corresponding amplitude and frequency. With the help of a mixer in NQR thermometer, measuring signal can be converted from high- to low-frequency signal without changing the amplitude of low-frequency signal. After this transformation, low-frequency measuring signal can be submitted to analog - digital conversion, i.e. ADC.

Currently there is a large number of ultra high bit ADC that enables us to extreme - accurately determine the change of probing signal amplitude. In NQR thermometer case, it was selected ADC with resolution of 32 bits that would satisfy the need for detection of signal change with a very small quantization step.

ADC will determine the signal change (amplitude) and send it to the microprocessor, which with a known algorithm will calculate the current value of the temperature. Also, to keep the thermometer in "tracking mode temperature", the feedback should be created by using this microprocessor, which will always adjust the frequency of the signal from the DDS and oscillating circuit parameters, above all capacitance, in the resonance with the frequency of the energy transitions of potassium chlorate nuclei, and will act as a servo system. The microprocessor will output the necessary data to PC via USB - port and/or display the temperature value on the display of device.

To implement this scheme following elements were chosen: digital signal synthesizer (DDS) AD9912, mixer (Mixer) AD831, analog - digital converter (ADC) ADS1282. The question of ordering of microprocessor (MCU) series STM32F40x is discussed.

The figure above represents a structure scheme of the NQR thermometer. In the subsequent implementation of the thermometer may appear some modifications and improvements, that's why the circuit can partly change its original look.

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