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The Nuclear Quadrupole Resonance and Sensory Properties of GaSe and InSe Layered Semiconductors

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The temperature and pressure dependences of NQR in indium and gallium monoselenides are studied by means of pulse NQR radiospectroscopy with a fast Fourier transform of the spin induction signals. An experimental installation pulse NQR method based on multi-functional software-controlled digital processing core is implemented in the FPGA Altera Cyclone. It was found from NQR spectra of ^{69}Ga and ^{115}In isotopes that semiconductor GaSe and InSe compounds can be used when creating the temperature sensors in the range of 20÷130 °C. For crystals investigated the accuracy of the temperature determination is ± 0.05 °C. It was found that the use of these layered compounds for measuring uniaxial pressure using NQR is possible at pressures up to 50÷100 kg/cm^2, where the manifestation of the hysteresis is not significant.

Keywords: Nuclear quadruple resonance, FPGA, InSe, GaSe, Temperature and pressure sensors.

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1. INTRODUCTION

Development of sensors of physical quantities based on semiconductor materials is an important direction of micro- and nanoelectronics [1-6]. The need to implement sensors of temperature, pressure, moisture, magnetic and electromagnetic fields in the form of multi-functional compact sensors is conditioned by a wide range of their applications. These devices are the basis for creation of distributed sensor networks. Layered semiconductor materials have received a special attention at the present stage of the development of semiconductor sensorics as a promising material for realization of solid state electronic devices [7, 8]. The most well-known measurement methods of physical quantities are based on the resistive, acoustic, optical, piezoelectric, Hall and other phenomena. A low reproducibility of the measured values and the need of periodic calibration and metrological verification are a common drawback of the most of them. Creation of new methods, which are free of the above-mentioned disadvantages, is an actual problem of semiconductor sensorics. This problem can be solved by the creation of sensors based on the nuclear quadrupole resonance (NQR) phenomenon in a number of layered semiconductor compounds, in particular, indium and gallium monoselenides [2]. Combination of sensitive NQR signal-recording equipment and sensory properties of InSe and GaSe crystals provides the implementation perspective on their basis of time-stable high-precision sensors which do not require periodic calibration. Moreover, the stated compounds are characterized by the resistance to ionizing radiation. Just the NQR method has the greatest prospect here, since it is one of the most sensitive investigation methods of the intramolecular structure of substances and their physical and chemical properties.

With changing temperature and pressure, a wide frequency range gives the possibility to realize high resolution of measuring devices based on NQR. The sample volume and mass play an important role in the case of the thermometer, since the increase in the temperature gradient of the sample and expansion of the NQR resonance line occur at large volumes leading to the decrease in the accuracy of temperature measurement [5, 9].

In this work, we present the results of a comprehensive study of a general technique of implementation of NQR-sensor equipment based on layered InSe and GaSe crystals and investigation of the temperature and pressure dependences of NQR in these compounds.

2. EXPERIMENTAL NQR METHOD

The NQR-sensor based on layered semiconductors is a crystalline sample placed in an oscillator circuit of the NQR spectrometer and frequency capturing and tracking system of the selected line of the resonance spectrum. Both the perfection of the sample crystal structure and qualitative parameters of the receiving and transmitting equipment directly influence the accuracy of the measured parameters. Therefore, a great attention is devoted to the noise and signal characteristics of the electron part of NQR-sensors.

Both the stationary technique and the pulse one with a fast Fourier transform (FFT) of the spin induction signals are used when creating temperature and pressure NQR sensors.

The principles of operation of the autodyne temperature sensor proposed by us are described in [10], where the balanced circuit of the spin-detector is used to improve the noise and signal characteristics. This solution allowed to increase the sensitivity compared with the asymmetric circuits and, correspondingly, on account of the decrease in the substance mass with the temperature dependence of the NQR frequency (Cu_2O) to 0.2 g led to the increase in the sensor sensitivity by 5÷10 %.

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Utilization of the stationary technique of the NQR observation has certain limitations associated with a significant time of the experiment (~ 30 min.). The pulse method with FFT, which has a substantial advantage in the time of the experiment [11], was used in order to perform the study of the temperature and pressure dependences of NQR in indium and gallium monoselenides. The structure of the proposed experimental equipment is illustrated in Fig. 1.

The feature of the proposed facility is its implementation based on the multi-functional software-controlled digital processing core. The imitation model (Fig. 2) and algorithms for operation of the basic units of NQR pulse spectrometer in one module based on the programmable logic integrated circuit (PLIC) EP1C6Q240C8 of FPGA Altera Cyclone [12] are developed in terms of modeling syntax of the logic structure dynamic modes. All stages of the device design starting from the SPICE-modeling of the scheme to the 3D image of the physical prototype (Fig. 3) are implemented by CAD Altium Designer.

Direct digital synthesizer (13) based on 48-bit phase accumulator with the possibility of speed frequency and phase manipulations [13] is the source of the carrier frequency. It provides the formation of NQR excitation

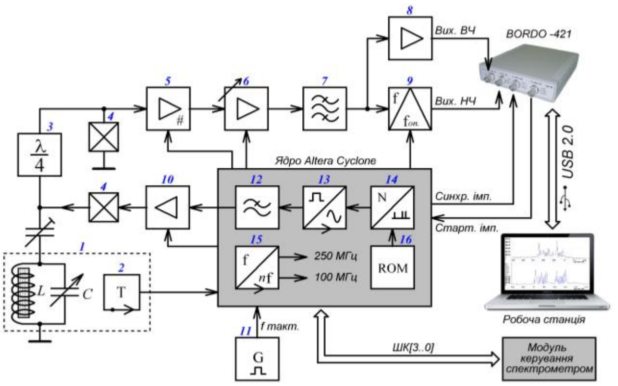

Fig. 1 – Experimental facility of the pulse method of observation of NQR with FTT of the spin induction signals: 1 – measuring cell; 2 – temperature sensor in the cell; 3 – λ/4-cable; 4 – diode limiters; 5 – gated amplifier; 6 – attenuator; 7 – bandpass filter; 8 – RF matching amplifier; 9 – synchronous detector; 10 – RF power amplifier; 11 – clock generator; 12 – low-pass filter (LPF); 13 – frequency synthesizer; 14 – pulse pattern former; 15 – frequency multiplier; 16 – memory block

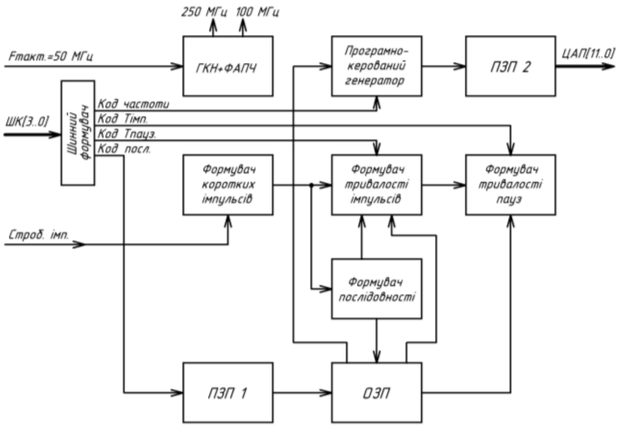

Fig. 2 – Structural scheme of the imitation model of the digital processing core

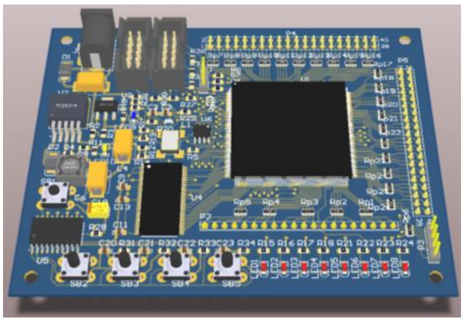

Fig. 3 – Digital processing core of the experimental facility of the pulse method of NQR observation implemented on PLIC EP1C6Q240C8

pulses in the frequency range of 1÷80 MHz. The carrier-oscillation frequency setting step is approximately equal to $\Delta f_{out} \approx 1 \times 10^{-6}$ Hz. Pulse sequence programmer provides the formation of 90-th excitation pulses of the duration of 0.1÷20 μs and the repetition period of 0.1 μs. The period between excitation pulses is controlled in the range of 0.1 μs÷1 s. Other lengths of time, for example, in the Carr-Purcell sequence [14]; length of 180-th pulses and periods between them is established automatically according to the selected program recorded in non-volatile memory ROM1. The data about the carrier-oscillation frequency, duration of the 90-th excitation pulse, period between pulses and sequence type comes from the spectrometer control unit to the digital processing core by a 4-bit control bus.

The analog path of the facility is implemented in the form of the functionally complete transmission-reception path containing broadband power amplifier (10), gated amplifier (5) and resonance signal detection channel. The initial broadband power amplifier represents a high-frequency transmitter loaded on the *LC*-circuit (1), in the coil of which the studied substance is placed. Amplifier allows to increase in the coil power δ-like pulses with the initial pulse power of 500 W.

Synchronous detection channel (9) is developed based on the balanced mixer SA612 [15].

Digital USB- oscilloscope "BORDO-421"with the software providing functions of a FFT and multiple storage was used to process the response signals of the nuclear spin system response with subsequent extraction of the NQR spectrum. The interval between measurements is specified by the frequency of start pulses coming from the DAC output of the digital oscilloscope.

3. TEMPERATURE AND PRESSURE NQR DEPENDENCES IN GaSe AND InSe

Gallium and indium monoselenides possess isotopes (^{69}Ga, ^{71}Ga, ^{113}In, ^{115}In) causing NQR in the crystals with anisotropic structure. NQR frequency is determined by the fundamental constants of the crystal. If pressure on the sample is constant, then resonance frequency is the function of temperature. Monocrystalline samples for investigations are obtained by the Bridgeman method. The long-term annealing with a gradual decrease in the annealing temperature is applied in order to improve the structural perfection and order polytypes [16].

The resonance spectra for the isotopes ^{69}Ga in GaSe and ^{115}In in InSe recorded by the pulse NQR method with a FFT are shown in Fig. 4 and Fig. 5, respectively. The study was carried out as a result of the action of an excitation pulse with the duration of 3 μs and power of 250 W. Temperature of spectra registration is $T = 20$ ºC. Temperature measurements consist in the tracking of the central frequency of the multiplet spectral line with the maximum intensity. As seen from the experimental results, a significant dependence of the NQR frequency on the temperature is manifested in the crystals of the studied monoselenides.

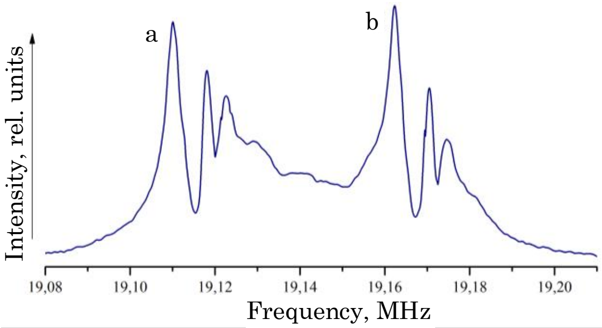

Fig. 4 – Experimental NQR spectrum of ^{69}Ga in GaSe

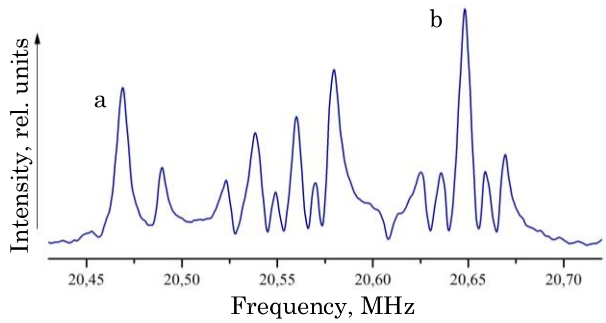

Fig. 5 – Experimental NQR spectrum of ^{115}In in InSe for the spin transition on the frequency of 20.5 MHz

Investigation results of the temperature dependence of the NQR frequency for both resonance spectral lines of GaSe and InSe are illustrated in Fig. 6 and Fig. 7. It is established that for GaSe the frequency-temperature linear transform with the slope of 1.54 kHz/deg is proper to the temperature range of 20÷130 ºC. Transform with the slope of 2.35 kHz/deg, which is linear in the temperature range of 20÷100 ºC, is observed for InSe. The temperature accuracy is equal to ± 0.05 ºC for both studied crystals. This is conditioned by the width of the resonance spectrum line and absolute temperature value. Accuracy increases to ± 0.025 ºC with decreasing temperature. This is explained by the decrease in the width of the resonance spectrum lines. High frequency-temperature transformation coefficients allow to use the studied semiconductor compounds as a thermometric substance for high-accuracy temperature sensor based on NQR.

A uniaxial pressure $F \| c$ is applied for the observation of the pressure dependence of NQR in the layered GaSe and InSe crystals. Layered GaSe and InSe crystals were placed inside the measuring cell which is a solenoid coil of the radio spectrometer oscillation circuit. The samples were manufactured in the form of packages of the layered crystal with sizes of 7 × 8 mm^2 and thickness of 3 mm, which is clamped between two rigid sapphire plates.

The resonance signal of ^{69}Ga was steadily attenuated with increasing uniform pressure to the plane of the layered package of crystalline GaSe. The change in the spectral intensity in the sample is illustrated in Fig. 8.

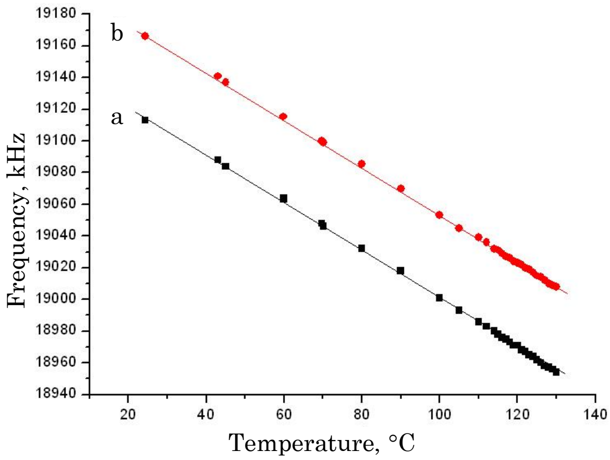

Fig. 6 – Frequency-temperature transformation obtained for the NQR spectrum of ^{69}Ga in GaSe

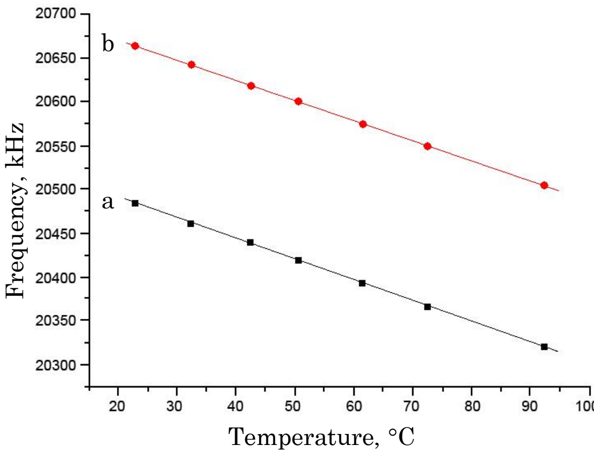

Fig. 7 – Frequency-temperature transformation obtained for the NQR spectrum of ^{115}In in InSe

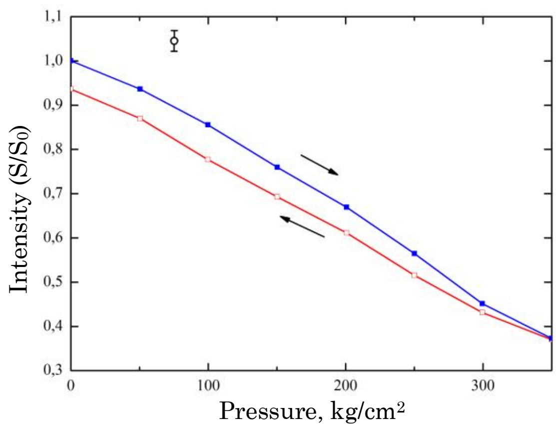

Fig. 8 – Dependence of the peak intensity of the resonance "a" line for the NQR spectrum of ^{69}Ga in GaSe with increasing and decreasing pressure on the sample

A convenient third transition (± 5/2 ↔ ± 7/2) with the frequency of ≈ 30.5 MHz is chosen instrumentally for the observation of the pressure dependence of NQR in InSe.

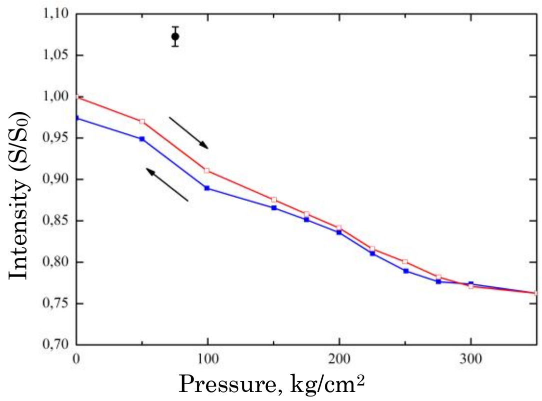

Fig. 9 – Dependence of the peak intensity of the resonance "a" line for the NQR spectrum of ^{115}In in InSe with increasing and decreasing pressure on the sample

In Fig. 9 we show the change in the NQR spectrum intensity on the applied pressure at the constant temperature of 25 ºC. It is established that deviation from the linear dependence in the range of 250÷350 kg/cm^2 is conditioned by noises when reducing the signal/noise level with increasing pressure. The effect is more noticeable in the calculation of the spectrum area. Decrease in the resonance signal intensity is associated with the formation of defects and appearance of the strain with increasing pressure on the crystal.

Constancy of the crystal structure under the action of a uniaxial pressure in the specified range is an important feature of GaSe and InSe compounds when measuring the NQR spectra.

4. CONCLUSIONS

The temperature and pressure dependences of NQR in indium and gallium monoselenides by the pulse NQR radio spectroscopy with a FFT of the spin induction signals have been studied.

The experimental facility of the pulse method of the NQR observation based on the multi-functional software-controlled digital processing core has been proposed for the investigations.

It is shown that semiconductor GaSe and InSe compounds can be applied in the creation of temperature and uniaxial pressure sensors using NQR.

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