*JOURNAL OF NANO- AND ELECTRONIC PHYSICS*
Vol. **13** No 5, 05030(5pp) (2021)

*ЖУРНАЛ НАНО- ТА ЕЛЕКТРОННОЇ ФІЗИКИ*
Том **13** № 5, 05030(5cc) (2021)

# The Use of Marginal Oscillator Detector with Increased Conversion Linearity for Recording Broadband Multiplet Nuclear Quadrupole Resonance Spectra

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(Received 21 July 2021; revised manuscript received 20 October 2021; published online 25 October 2021)

This paper describes the features of choosing the sweep method and mode in the study of broadband multiplet nuclear quadrupole resonance (NQR) spectra using a marginal oscillator sensor with increased conversion linearity. In particular, the work of the improved sensor in the frequency sweep mode is considered when using: bipolar frequency modulation with synchronous second harmonic detection; Zeeman modulation with synchronous first harmonic detection, provided that the modulation depth is much greater than the line width; Zeeman modulation with synchronous second harmonic detection. Much attention is paid to experimental studies of the NQR spectra and the orientation dependence of the relative integral intensity of their resonance lines for three multiplet groups in the frequency range 20.4-20.7 MHz of the $3/2 \leftrightarrow 5/2$ $^{115}$In quadrupole junction in a semiconductor layered InSe compound grown by the Bridgeman method. It is established that to obtain the optimal signal amplitude, the shape of the modulating field must be square-rectangular. The performed NQR studies in InSe confirm the complexity of the problem of polymorphism in layered crystals, which requires further research using various experimental techniques.

**Key words**: NQR, Sensors, Modulation, Layered semiconductors, Multiplet spectra.

DOI: 10.21272/jnep.13(5).05030 PACS numbers: 76.60. – k, 76.60.Gv

## 1. INTRODUCTION

Semiconductor crystalline compounds of the $A^3B^6$ group, which includes gallium and indium monoselenides, are widely used in the development of qualitatively new and modern semiconductor devices such as photodiode structures, Schottky barriers, MIS devices, and heterojunctions [1-5]. The layered structure of these compounds leads to significant anisotropy of crystals and determines many features of their physical properties [5, 6]. In particular, the presence of polytypism requires a detailed study, which is a problem both in the theoretical aspect and in the practical use of devices based on the aforementioned semiconductor materials [1, 7].

Nuclear quadrupole resonance (NQR) is one of the few experimental methods, the use of which makes it possible to determine the perfection of layered semiconductor crystalline compounds in the process of technological heat treatment as the spectra are ordered and resolved [8]. The presence of many polytypic modifications in the crystal structure leads to the creation of a kind of molecular framework in the volume of the crystal, which manifests itself in the appearance of multiplets in the NQR spectra, the frequency range of which is almost hundreds of kilohertz [9].

The NQR method is based on the absorption of the energy of radio frequency (RF) waves by changing the orientation of the quadrupole moments of atomic nuclei in an inhomogeneous electric field created by charges external to the nucleus [10]. The levels of quadrupole energy in a solid arise from the interaction of quadrupole moments with an inhomogeneous electric field at the location of the resonating nucleus; therefore, the NQR spectrum reflects the electron density distribution near a particular atom. This is the uniqueness of the NQR method in the study of fine structural features of chemical compounds.

Experimental methods for observing NQR resonant frequencies are divided into continuous and pulsed. In the continuous technique, the test substance is irradiated with an alternating RF field. When passing through the resonant frequencies, the energy absorption of this field by quadrupole nuclei is measured. The main feature of the method is to sweep the resonance spectrum by scanning the frequency. The simplicity of this detection technique and the wide range of isotopes studied by adjusting the autogenerator frequency play a crucial role when choosing a continuous NQR sensor in the study of broadband multiplex NQR spectra of layered semiconductor crystalline compounds. At the same time, the issue of temperature studies in NQR is also relatively easy to solve.

## 2. MODULATION METHODS IN NQR RADIOSPECTROSCOPY

To achieve the goal of the work, it is proposed to improve the marginal oscillator method of recording the NQR signal for studying broadband spectra [11]. The purpose of improving the device was to increase the noise immunity of the marginal oscillator while maintaining its sensitivity, reducing the distortion of the shape of the spectra arising from the baseline drift and eliminating the nonlinearity of the scale during frequency sweep. Such distortions are standard for a typical NQR sensor with a marginal oscillator detector. The block diagram of the experimental installation of a continuous NQR sensor, used by us to implement the method of synchronous detection of resonance signals in the sweep mode, is shown in Fig. 1. A detailed structural and functional diagram of the upgraded NQR marginal oscillator detector is considered in [11].

The test sample in the form of a powder or a single

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crystal is placed in the marginal oscillator coil with frequency modulation. The NQR phenomenon determines the electrical signal at the detector output, associated by a certain law with polarization (displacement). When modulating the resonance zone, one can observe the modulation of the RF voltage by the resonance signal. To implement the modulation method for observing spectral lines in NQR, an additional frequency modulation $\omega_m$ is superimposed on the carrier frequency $\omega_0$. In this case, in spectrometers of wide lines, to prevent distortions of the line shape, the modulation frequency $\omega_m$ is taken less than the width of the resonance line of the spectrum under study. The modulation frequency, as a rule, lies in the low frequency range and does not exceed the range of 150-200 Hz.

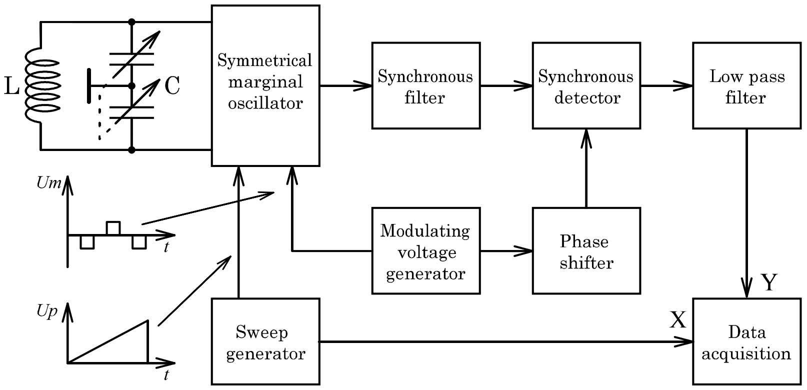


**Fig. 1** – Implementation of the NQR synchronous detection method in the sweep mode

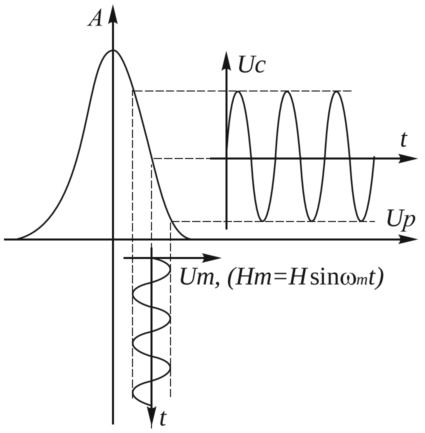


**Fig. 2** – Illustration of the method of differential passage of the NQR resonance line

The appearance of a periodic signal at the marginal oscillator output when passing through the NQR resonance line is illustrated in Fig. 2.

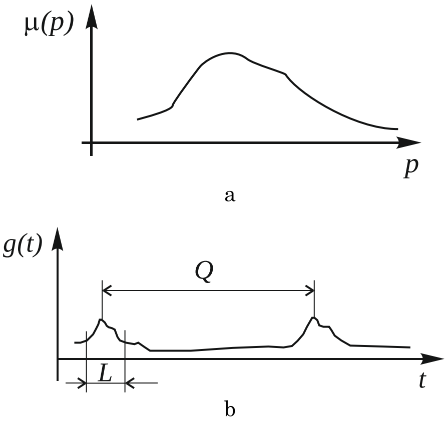
Since the line shape characteristic is a nonlinear function, the output voltage is not purely harmonic. The composition of such an alternating voltage includes frequency components that are multiples of the modulation frequency $\omega_m$. This allows the detection of the spectral line on the first, second, etc. harmonic component. In this way, it is possible to select the first, second, etc. derived function, respectively, at the output of the synchronous detector. The derivative number is determined by the choice of the reference voltage frequency that drives the synchronous detector.

The sweep generator makes it possible for a certain period of time to set the bias voltage on the varicap of the marginal oscillator and register the signal from its output as a function of bias. The level of resonance signals is usually small, and the detector makes significant noise. Therefore, in this case, synchronous detection is used.

## 3. ANALYSIS OF THE SWEEP MODE

When analyzing a physical phenomenon, the signal coming to the detector will have a variable amplitude and frequency that is slightly different from the carrier $\nu_0$ due to the sweep. Let us consider a physical phenomenon that gives a signal $\mu(p)$ at the detector as a function of the displacement $p$ (Fig. 3a).

To simplify the analysis, we will assume that the sweep is periodic with a repetition period greater than the duration of the phenomenon (Fig. 3b). Therefore, it is possible to introduce the sweep rate when expanding the function $g(t)$ in a Fourier series. If the sweep changes the signal $x$ linearly, one can get the law $y = \mu(p)$.



a

b

**Fig. 3** – Bias function $\mu(p)$ (a), waveform timing in the sweep mode (b)

Suppose that the sweep is periodic with a period $T$, which exceeds the interval $T_0$, beyond which $y = 0$. The recoverable periodic signal $g(t)$ is expanded into a Fourier series with an interval between two successive frequencies equal to $1/T$.

Suppose that the sweep without modulation is carried out according to the law $x = \upsilon t$ and with modulation according to the law $\upsilon t + \beta\cos 2\pi\nu_0 t$. Let us also assume that the frequency $\nu_0$ is so high that $y$ changes insignificantly over a time corresponding to a large number of sweep periods. Then one can represent $y(p)$ in the vicinity of $p_0$ by the Taylor series

$$y(p_0+\Delta p) = y(p_0) + \Delta p \left.\frac{dy}{dp}\right|_{p=p_0} . \qquad (1)$$

If $p_0 = \upsilon t_0$ and $\Delta p\beta\cos(2\pi\nu_0 t)$, then

$$y\left[\upsilon t_0 + \beta\cos(2\pi\nu_0 t)\right] = y(\upsilon t_0) + \beta\left(\left.\frac{dy}{dp}\right|_{p=p_0}\right)\cos 2\pi\nu_0 t \qquad (2)$$

Hence it follows that the coefficient $\beta$ should be small enough, so that the value $\frac{\beta^2}{2}\left.\frac{d^2y}{dp^2}\right|_{p=p_0}$ can be neglected as compared to $\beta\left.\frac{dy}{dp}\right|_{p=p_0}$. As a result of detection, we obtain

$$\lim_{T\to\infty}\frac{1}{T}\int_{t_0}^{t_0+T} y\left[\upsilon t_0 + \beta\cos(2\pi\nu_0 t)\right]\cos(2\pi\nu_0 t)dt , \qquad (3)$$

which is equivalent to

$$\lim_{T\to\infty}\frac{1}{T}\int_{t_0}^{t_0+T} y(\upsilon t_0)\cos(2\pi\nu_0 t)dt +$$
$$+\lim_{T\to\infty}\frac{1}{T}\int_{t_0}^{t_0+T} \beta\left[\cos(2\pi\nu_0 t)\right]^2\left(\left.\frac{dy}{dp}\right|_{p=p_0}\right)dt . \qquad (4)$$

As long as the value of $y(\upsilon t_0)$ is constant, the first integral is equal to zero, and the previous expression (4) takes the form

$$\lim_{T\to\infty}\frac{1}{2T}\int_{t_0}^{t_0+T} \beta\left(\left.\frac{dy}{dp}\right|_{p=p_0}\right)\left[1+\cos(4\pi\nu_0 t)\right]dt = \frac{1}{2}\beta\left.\frac{dy}{dp}\right|_{p=p_0} . \qquad (5)$$

So, we got not $y = f(p)$, but the derivative $dy/dp$. In so doing, it was assumed that the modulation depth $\beta$ is small enough to neglect the value of $\frac{\beta^2}{2}\left.\frac{d^2y}{dp^2}\right|_{p=p_0}$.

Let $Y(\lambda)$ be the Fourier map of the function $y = \mu(p)$ (in this transformation, the variable $p$ corresponds to the variable $\lambda$) and $-\Delta\lambda$, $+\Delta\lambda$ is the spectral band occupied by $Y(\lambda)$.

Then the Fourier map of the derivative function $y = \mu(p)$ will occupy the same spectral interval, since the Fourier map from $dy/dp$ is $2\pi j\lambda Y(\lambda)$.

If the sweep along the $p$ axis from 0 to $p_0$ is carried out in $p_0$ seconds at a constant speed, then $y = \mu(p)$ corresponds to $y = \mu(t)$, the sweep speed is equal to one, $y = \mu(t)$ has the Fourier map $Y(\nu)$ in the spectral range $\pm\Delta B$, $\Delta\lambda$ and $\Delta B$ are expressed by the same number.

If the sweep was carried out not in $p_0$, but in $\theta$ seconds, the sweep speed would be $\upsilon = p_0/\theta$. Instead of $y(t)$, we get the function $y(t/\upsilon)$, the Fourier map of which is the function $\upsilon Y(\upsilon\nu)$, which occupies the spectral interval $\pm\Delta B'$, and $\Delta B' = \upsilon\Delta\lambda$.

If $T$ is the duration of the integration interval (in the case of a low-pass filter, $T$ is replaced by $2\tau$, where $\tau$ is the filter time constant) in the above case and $\pm B$ is the spectral noise bandwidth, then the power gain due to synchronous detection is $2W$, and to preserve the $dy/dp$ value without distortions, it is necessary to have $T \le \alpha B/\upsilon\Delta\lambda$. If $T = \alpha B/\upsilon\Delta\lambda$, then the limit gain value is equal to $2\alpha B/\upsilon\Delta\lambda$. It follows that the longer the sweep time, the more gain can be obtained.

## 4. RESEARCH ON $^{115}$In NQR SPECTRA

Experimental studies of $^{115}$In NQR spectra in InSe semiconductor compound grown by the Bridgman method were carried out using an NQR sensor with increased conversion linearity [9, 11]. The sample under study with dimensions of 10 × 10 × 10 mm$^3$, fixed in the container of the rotating mechanism inside the coil, rotated relative to the induction vector $B_1$ of the magnetic field. Fig. 4 shows the placement of sample under study in the marginal oscillator coil.

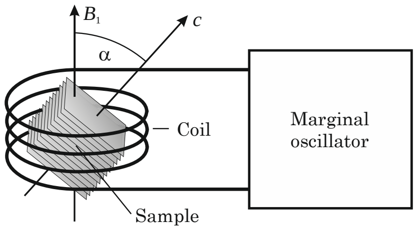


**Fig. 4** – Placement of sample in the marginal oscillator coil

In InSe, for the $^{115}$In isotope, four resonance frequency regions were found, whose average values (10.25, 20.5, 30.8, and 41 MHz) approximately satisfy the ratio 1:2:3:4 [1, 9]. The latter indicates an insignificant asymmetry of the electric field gradient at $^{115}$In, and its distribution can be considered axially symmetric. Fig. 5 shows the $^{115}$In NQR spectra in a crystalline InSe sample with a volume of 1 cm$^3$. The spectra were recorded for the 3/2 ↔ 5/2 $^{115}$In quadrupole junction in the frequency range of 20.4-20.7 MHz.

The spectrum in Fig. 5a was recorded by bipolar frequency modulation with a frequency deviation of no more than ± 1 kHz. The atomic layers of the crystal are located in the marginal oscillator coil along the direction of the RF field, that is, $B_1 \perp c$ ($c$ is the main optical axis). In this case, the signal intensity is maximum. Fig. 5b shows the $^{115}$In NQR spectrum in InSe recorded by the Zeeman modulation method at a temperature of 293 K. In this case, a bipolar pulsed magnetic field up to 0.01 T was applied to the sample. Increasing the induction of the magnetic field makes it possible to investigate wider spectra and at the same time to register the initial lines of resonance absorption. The spectrum in Fig. 5c is obtained by the Zeeman modulation method with synchronous second harmonic detection.

As seen from the spectra in Fig. 5, the use of frequency modulation with a bipolar voltage waveform ensured the elimination of baseline drift when registering a complex multiplet spectrum. At the same time, maintaining the shape of the current in the coils using a modulating amplifier based on a voltage-controlled current source circuit provided a fine registration of resonance lines without their significant expansion.

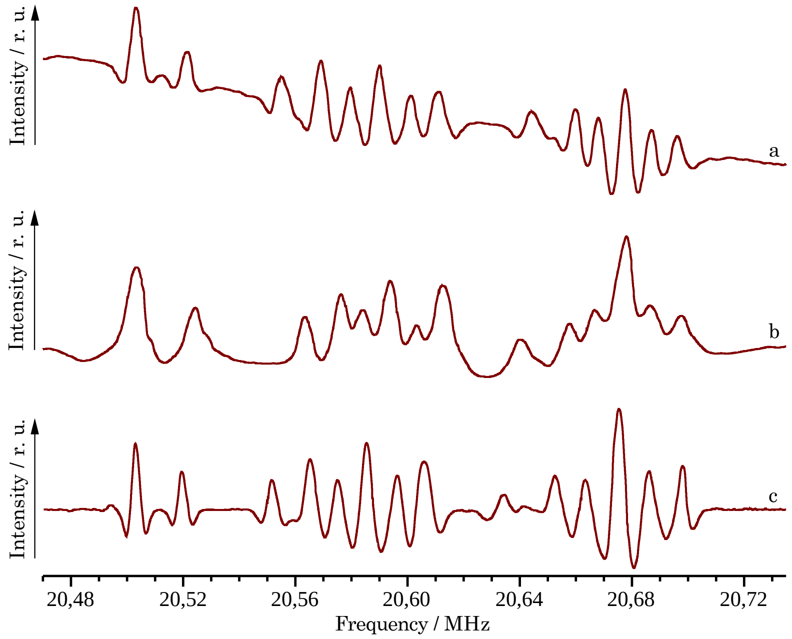


**Fig. 5** – The $^{115}$In NQR spectra in single-crystal InSe: recorded by bipolar frequency modulation with synchronous second harmonic detection (a), obtained by Zeeman modulation with synchronous first harmonic detection, provided that the modulation depth is much greater than the line width (b), obtained by Zeeman modulation with synchronous second harmonic detection (c)

In addition to the above, Zeeman modulation has another significant advantage. When using frequency modulation, we are forced to take the modulation amplitude less than the linewidth, which leads to a loss of intensity. However, using Zeeman modulation, under the same conditions, a better signal-to-noise ratio can be obtained.

Using the NQR method, the dependence of the spectrum intensity on the orientation of the crystallographic axes of an anisotropic crystal with respect to the vector of the magnetic component of the high-frequency field is investigated [12]. In fact, the two-dimensional crystal structure of monoselenide compounds makes it possible by the NQR method to orient the crystal along the selected coordinate system and, moreover, to reveal the features associated with the violation of the crystal symmetry, that is, structural defects.

Fig. 6 shows orientation plot of the relative integral intensity of resonance lines for three multiplet groups of the spectrum shown in Fig. 5c. For all lines of the spectrum, the dependence of the intensity on the direction of the vector $B_1$ relative to the crystallographic axis $c$ is observed. It was found that the maximum of the resonance intensity really corresponds to the case when $B_1 \perp c$ ($\alpha = 90^{\circ}$, Fig. 6). If $B_1 \| c$, ($\alpha = 0^{\circ}$, Fig. 6), the resonance intensity decreases to minimum values for all multiplet groups 1, 2, 3, which confirms the fact that in this single-crystal ingot, In-Se-Se-In monatomic layers are located along the direction of crystal growth. The final signal will be due to both the misorientation of the atomic multilayers and the inhomogeneity of the $B_1$ flow due to the finite dimensions of the solenoid. The shape of the multiplet of resonance lines is very sensitive to distortions of the crystal periodicity, the presence of deformation, or the presence of an impurity. Defects in the crystal structure can be caused, for example, by a violation of the technological modes for the preparation of the starting materials, in particular, by the instability of the crystal growth temperature or an incorrect temperature mode of its annealing.

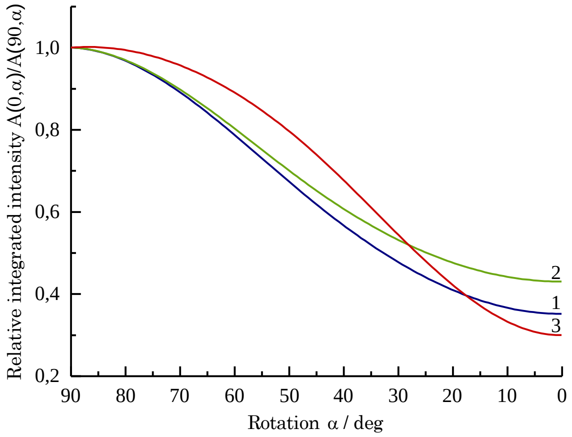


**Fig. 6** – Orientation plot of the intensity of NQR lines in InSe sample for multiplet groups in the range of 20.45-20.52 MHz (1), 20.51-20.60 MHz (2), 20.60-20.70 MHz (3)

## 5. CONCLUSIONS

Compared to frequency modulation, Zeeman modulation demonstrates better results for quadrupole nuclei located in the axial gradient of the electric field, which is inherent in InSe crystals. It is established that Zeeman modulation has the following advantages in comparison with other modulation methods:

1) only NQR signals are modulated, while piezoresonances and radio interference are excluded;

2) the absorption line is observed, rather than its derivatives;

3) no additional adjustments and changes to the marginal oscillator circuit are required;

4) modulation does not affect the frequency measurement method.

The latter is especially important in NQR to determine the frequency when recording complex spectra with narrow lines. To obtain the optimal signal amplitude, the shape of the modulating field must be square-rectangular. If the polarity of the modulating field pulses is changed, then the background synchronous signals are attenuated at odd harmonics of the modulation frequency.

The complex but ordered nature of the $^{115}$In NQR spectra in InSe is most likely due to the presence of structural defects. The performed studies of NQR in InSe confirm the complexity of the problem of polymorphism in layered crystals, which requires further investigation using various experimental techniques.

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# Застосування автодинного сенсора з підвищеною лінійністю перетворення для реєстрації широкосмугових мультиплетних спектрів ядерного квадрупольного резонансу

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У роботі описуються особливості вибору методики та режиму розгортки при дослідженні широкосмугових мультиплетних спектрів ядерного квадрупольного резонансу (ЯКР) із застосуванням автодинного сенсора з підвищеною лінійністю перетворення. Зокрема, розглядається робота удосконаленого сенсора у режимі розгортки за частотою при використанні: біполярної частотної модуляції із синхронним детектуванням по другій гармоніці; модуляції Зеемана із синхронним детектуванням по першій гармоніці при умові, що глибина модуляції набагато більша за ширину лінії; модуляції Зеемана із синхронним детектуванням по другій гармоніці. Велика увага приділяється експериментальним дослідженням спектрів ЯКР та орієнтаційної залежності відносної інтегральної інтенсивності їх резонансних ліній для трьох мультиплетних груп у частотному діапазоні 20,4-20,7 МГц квадрупольного переходу $^{115}$In 3/2 ↔ 5/2 в напівпровідниковій шаруватій сполуці InSe, вирощеній методом Бріджмена. Встановлено, що для отримання оптимальної амплітуди сигналу форма модулюючого поля повинна бути квадратно-прямокутною. Проведені дослідження ЯКР в InSe підтверджують складність проблеми поліморфізму в шаруватих кристалах, яка потребує подальшого дослідження із залученням різних експериментальних методик.

**Ключові слова**: ЯКР, Сенсори, Модуляція, Шаруваті напівпровідники, Мультиплетні спектри.