Investigations on temperature dependences of parameters of ^{127}I NQR spectrum of $(BiI_3)_{(1-x)}(PbI_2)_x$ mixed layered semiconductor and alkaline halogens crystals

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Results of investigations of the temperature dependence of NQR frequencies in the temperature range of 4.2–150 K for ^{127}I and ^{79}Br of the $(BiI_3)_{(1-x)}(PbI_2)_x$ mixed layered semiconductor and the crystals of alkaline halogens are presented. The abnormally large absolute values of temperature coefficients of the NQR frequency for $(BiI_3)_{(1-x)}(PbI_2)_x$ have been detected. It can be explained by influence of the point charges and interlayer fluctuations. It is concluded that the quasi-two-dimensional nature of the vibration states at PbI_2 contents of $x \leq 0.08$ is persistent. The value of the orientation and translational vibrations frequency of the halogen ions assuming the correctness of the two-frequency model Bayer-Kushida has been calculated.

Keywords: nuclear quadrupole resonance, layered semiconductors, asymmetry parameter, nanoclusters, alkaline halogens crystals.

Приведены результаты исследований температурных зависимостей частот ЯКР ^{127}I и ^{79}Br смешанного слоистого полупроводника $(BiI_3)_{(1-x)}(PbI_2)_x$ и кристаллов щелочных галогенатов $RbJO_3$ и $KBrO_3$ в интервале температур 4,2–150 К. Обнаружено аномально большие показатели абсолютных значений температурных коэффициентов частоты ЯКР для $(BiI_3)_{(1-x)}(PbI_2)_x$, которые можно объяснить влиянием межслоевых колебаний и колебаний точечных зарядов решетки. Сделан вывод о сохранении квазидвумерного характера колебательных состояний в области содержания PbI_2 $x \leq 0,08$. Рассчитано значения частот ориентационных и трансляционных колебаний галогенат-ионов в предположении двухчастотной модели Байера-Кушиды.

Дослідження температурних залежностей параметрів спектра ЯКР ^{127}I напівпровідника $(BiI_3)_{(1-x)}(PbI_2)_x$ та кристалів лужних галогенатів. *І.Г.Вертегел, Є.Д.Чесноков, О.І.Овчаренко, І.І.Вертегел, О.С.Іванов, Ю.П.Гнатенко, О.А.Понкратенко.*

Приведено результати досліджень температурних залежностей частот ЯКР ^{127}I та ^{79}Br змішаного шаруватого напівпровідника $(BiI_3)_{(1-x)}(PbI_2)_x$ та кристалів лужних галогенатів $RbJO_3$ і $KBrO_3$ в інтервалі температур 4,2–150 К. Виявлено аномально великі показники абсолютних значень температурних коефіцієнтів частоти ЯКР для $(BiI_3)_{(1-x)}(PbI_2)_x$, які можна пояснити впливом міжшарових коливань та коливань точкових зарядів гратки. Зроблено висновок про збереження квазідвумірного характеру коливальних станів в області вмісту PbI_2 $x \leq 0,08$. Розраховано значення частот орієнтаційних та трансляційних коливань галогенат-іонів у припущенні двухчастотної моделі Байера-Кушиди.

1. Introduction

In this work we study the temperature dependence of parameters of the spectrum of nuclear quadrupole resonance (NQR) layered semiconductors crystals $(BiI_3)_{(1-x)}(PbI_2)_x$ and isostructural crystals of alkaline halogens $RbJO_3$ and $KBrO_3$ related to ion-covalent crystals which have one structural unit in the elementary cell. Temperature coefficients of NQR spectrum parameters are highly sensitive to changes in crystals dynamic parameters (amplitudes, frequencies), that allows to study the dynamic characteristics by the NQR lattice [1, 2]. The relevance of studies of solid solutions of layered semiconductor crystals $(BiI_3)_{(1-x)}(PbI_2)_x$ is primarily associated with the possibility of formation of cluster structures in such crystals, which is a factor that significantly affects their properties. The BiI_3, CdI_2, and PbI_2 layered semiconductor materials have a number of important physical properties, which enable to use them as γ-radiation detectors with the high energy resolution. ^{127}I nuclear quadrupole resonance (NQR) spectra of chemically pure BiI_3 and PbI_2 ($x = 0$ and $x = 1$) crystals and mixed layered semiconductor $(BiI_3)_{(1-x)}(PbI_2)_x$ were studied in [3–7]. Absorption and reflectance spectra, as well as X-ray structural analysis of $(BiI_3)_{(1-x)}(PbI_2)_x$ mixed crystals, were studied in [8]. It is known [10–12] that temperature dependence of the NQR spectrum parameters can be used to analyze the long-wave phonon spectrum. In this work, firstly, on the base of our studies of the temperature dependence of the NQR spectrum parameters $(BiI_3)_{(1-x)}(PbI_2)_x$ and $RbJO_3$ and $KBrO_3$ the analysis of vibrational spectrum of these crystal has been carried out.

2. Experimental

^{127}I NQR spectra of $(BiI_3)_{(1-x)}(PbI_2)_x$ crystals under investigation were measured in the temperature range of 77–150 K and in the frequency range of 5–300 MHz using an quasi-coherent NQR spectrometer. Accuracy was determined by the half-width of the NQR frequency lines and for crystals of alkaline halogens it was no worse than ±3–5 kHz, while for $(BiI_3)_{(1-x)}(PbI_2)_x$ it was ±100 kHz. Crystals with PbI_2 contents of x =0.00, 0.05, 0.08, 0.20 and 0.30 were studied. Measurements of ^{127}I NQR frequencies ν′ and ν, corresponding to $\pm1/2\leftrightarrow\pm3/2$ and $\pm5/2\leftrightarrow\pm3/2$ transitions, enabled to determine the temperature and concentration dependence of the quadrupole coupling constans $e^2Qq_{zz}(x)$ and the asymmetry parameter η(x) of the electric field gradient tensor ($\eta = (q_{xx} - q_{yy})/q_{zz}$) (EFGT). The accuracy of determination of the asymmetry parameter and quadrupole coupling constant, dependent on the line width, was, respectively, no worse than ±1.5 % and ±0.1 % of their absolute values. At temperatures above the Debye temperature T_D, the NQR frequency usually exhibits a linear dependence [1]. When studying the temperature dependence of the frequency spectrum of

NQR lines ν′ and ν containing PbI_2 $x = 0,00$, 0,05, 0,08, 0,20, 0,30 in the temperature range of 77–150 K it was found that the NQR frequency of those lines varies linearly with temperature. The experimental results obtained for the NQR lines ν′ and ν made it possible to determine the temperature coefficients of the NQR spectrum parameters: $k_1 = d\nu_1/dT$, $k_2 = d\nu_2/dT$. The accuracy of the specified parameters determination was defined by the width of the NQR lines and precision of the sample temperature stabilization and was no worse than ±10 % for all lines. The data of our measurements are shown in Table and Fig. 1. In this work we present the results of the study of temperature dependences of the spectrum parameter I^{127} ($k_1 = d\nu_1/dT$, $k_2 = d\nu_2/dT$) in the mixed layered semiconductor $(BiI_3)_{(1-x)}(PbI_2)_x$ and crystals and alkaline halogens $RbJO_3$ and $KBrO_3$.

3. Results and discussion

It is known that for an intracrystalline field with asymmetry parameter η = 0 [1]

$$\nu_{(|m|\leftrightarrow m-1|)} = |\{3eQ\frac{q_{\overline{zz}}}{4hI(2I-1)} \cdot (2|m|-1)|,$$

where Q is nuclear quadrupole moment, e — electronchardge, I — the nucleus spin, m — quantum number, $q_{\overline{zz}}$ — the time-averaged EFGT, averaged by lattice vibrations. Note that q_{zz} is defined by contributions from the covalent bonds of an ion and from the point charges of the lattice ions q_{zz}^i [5]. It was shown [8, 9] that the temperature dependence of NQR frequency in the case of zero EFGT skewness parameter and if q_{zz}^i contribution from the point charges can be neglected and this may be used to interpret the long-wavelength low-frequency phonon spectra of crystals. The vibrations with frequencies not exceeding 200 cm^{-1} are the most effective in averaging q_{zz}. Spectra of crystal lat-

tices vibrations of alkaline halogens $RbJO_3$ and $KBrO_3$ are similar to the spectra of isolated halogen-ion, and the contribution of the lattice point charges can be neglected [9–10]. Therefore, for analysis of temperature dependence of the NQR frequencies in $RbJO_3$ and $KBrO_3$ the dual frequency averaging model GEF was used, which was obtained in the approximation of isolated halogen-ion oscillation [9]. Analysis of the temperature dependence of the NQR frequencies halogens alkaline crystals was carried out by method of least squares, using the software [13]. Varying the parameters ν_0, ν_1, ν_2, A_1^{-1} and A_2^{-1} of the Bayer-Kushida theory was carried out taking into account the "weight" of a standard error for different temperatures. Values of the inertial factors A_i^{-1} can be compared with the values of the moments of inertia halogen-ions which oscillate relative to axes X and Y of tensor GEF. Moreover, as the moment of inertia of translational oscillation the rotational moment of inertia anion $I_T = mr^2$ can be considered, where m — mass anion, r— average distance between cations and oxygen atoms of anion [9]. Using comparison of calculated values $A_1^{-1} = 145 \cdot 10^{-47}$ kg·m² and $A_2^{-1} = 1290 \cdot 10^{-47}$ kg·m² and $I_T = 1309 \cdot 10^{-47}$ kg·m² with moments of inertia $I_R = 144 \cdot 10^{-47}$ kg·m² and $I_T = 1309 \cdot 10^{-47}$ kg·m² relative to axes X and Y of tensor GEF, which were determined from the geometric dimensions of halogen-ions and their position in the lattice, it was concluded that frequency of 170 cm^{-1} and 85 cm^{-1} determined by temperature dependence of the NQR frequency crystals $RbIO_3$ should correspond to rota-
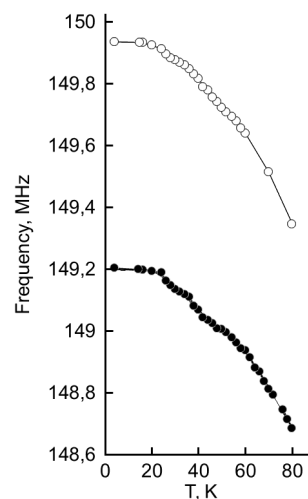

Fig. 1. Temperature dependences of NQR frequencies of I^{127} and Br^{79} crystals of alkaline halogens $RbJO_3$ — ● and $KBrO_3$ — ○. Points-experimental results, solid line-calculation.

tional and translational fluctuations of halogen-ions IO_3^-, respectively.

A similar analysis was carried out for crystal $KBrO_3$ for which the parameters of the Bayer-Kushida theory were determined. From the comparison of calculated values $A_1^{-1} = 128 \cdot 10^{-47}$ kg·m² and $A_2^{-1} = 1350 \cdot 10^{-47}$ kg·m² of $I_R = 129 \cdot 10^{-47}$ kg·m² and $I_T = 1313 \cdot 10^{-47}$ kg·m² calculated frequencies of 165 cm^{-1} and 110 cm^{-1} were attributed to the translational and rotational oscillations of the halohen-ions of BrO_3^-. The values obtained for the frequency orientation and translational vibrations of the halogen-ions correlate with the data of [10, 12], in which interpretation of the phonon spectra was performed on the basis of CD and the factor-

Table.

$(BiI_3)_{(1-x)}(PbI_2)_x$	k_1/ν_1 $(10^{-3}$ K$^{-1})$ $\pm1/2 \rightleftharpoons \pm3/2$	k_2/ν_2 $(10^{-3}$ K$^{-1})$ $\pm3/2 \rightleftharpoons \pm5/2$	η	e^2Qq_{zz}, MHz	Spectral lines
$x = 0.00$	-0.1402	-0.0819	0.29	682.18	*nuБN NAФ*
$x = 0.05$	-0.1543	-0.090	0.287	682.75	*nuБN NAФ*
$x = 0.08$	-0.1316	-0.089	0.285	682.97	*nuБN NAФ*
$x = 0.2$	*	-0.1523	0.15	684.011	*vprimeБs*
$x = 0.3$	*	-0.1754	0.15	684.005	*vprimeБs*
$RbJO_3$	-0.0129	*	0.014	991.5	*nuБN NAФ*$_1$
$KBrO_3$	-0.0171	*	*	*	*nuБN NAФ*$_2$

* The temperature dependence was not investigated.

group analysis of the Raman spectroscopy data.

For layered semiconductor crystals the contribution lattice point charges in the NQR frequencies temperature dependence can be significant [14], leading to inability to use the dual frequency model of averaging GEF. If symmetry of the EFGT differs from axial (for BiI_3 crystal, $\eta = 29$ %) for spin $I = 5/2$ the NQR frequency, eQq_{zz}, and η are related by solutions of the corresponding secular equations [15]. The absolute values of the NQR frequencies temperature coefficients in crystals of alkaline halogens are due mainly to fluctuations of isolated alkaline halogens, while in the layered crystals there are interlayer vibrations and oscillations of the crystal lattice point charges. Like PbI_2 and BiI_3 crystals, $(BiI_3)_{(1-x)}(PbI_2)_x$ layered crystals are characterized by structural anisotropy, which should leads to the vibrational states of quasi twodimensional character [6]. The vibrations that can effectively average the of electric field gradient in the studied crystals primarily include the low-frequency interlayer vibration associated with the weak interaction between the layers. The temperature coefficients of frequency (k_1 and k_2), for the line ν for $x = 0.05$ and $x = 0.08$ do not differ from those for pure BiI_3 ($x = 0$) by more than 17 %. Given the accuracy of determining the studied parameters (± 10 %), we can conclude that the experimental values at PbI_2 contents of $0 \leq x \leq 0.08$ remain constant. This suggests that, at $0 < x \leq 0.08$, the low-frequency interlayer vibrations undergo no significant changes and that inclusion of PbI_2 groups doesn't lead to the significant change in the twodimensionality degree of the crystal structure.

For BiI_3 crystals at 77 K with PbI_2 contents of $x = 0.20$ and 0.30, line ν' was observed in the ^{127}I NQR spectrum, the parameters of which are differed significantly from the parameters of the ^{127}I line ν for pure BiI_3 [5]. For example, at $x = 0.20$, the ν' line at 77 K is characterized by the following values of the parameters: $\nu_{\pm 1/2 \leftrightarrow \pm 3/2} = 104.35$ MHz, $\nu_{\pm 5/2 \leftrightarrow \pm 3/2} = 204.20$ MHz, $eQq_{zz}' = 684.01$ MHz and $\eta' = 0.15$.

It's important to note that the asymmetry parameter η for this new line ν' in the ^{127}I NQR spectrum decreases about twice: from $\eta = 0.29$ to $\eta' = 0.15$. Value of the constant $e^2Qq'_{zz}$ of the electric field gradient at ^{127}I nuclei does not change considerably herewith: $e^2Qq_{zz} = 682.18$ MHz and

$e^2Qq_{zz}' = 684.01$ MHz. We think that, with increasing x, the electric field gradient symmetry increases. It's necessary to note that the line υ of the ^{127}I NQR spectrum with $e^2Qq_{zz} = 682.18$ MHz and $\eta = 0.29$ in range $0.20 \leq x \leq 0.6$ is not observed.

The frequency temperature coefficients ($d\nu/dT$) increased in comparison with the line ν' (Table) for this new line ν in the NQR spectrum. For example, for the line ν' at $x = 0.30$ $d\nu/dT = -74.6$ KHz/K, whereas for the line ν at $x = 0$ $d\nu/dT = -15.3$ KHz/K. As a result, we can conclude that in the PbI_2 content range $0.20 \leq x \leq 0.6$ compared with range $0 \leq x \leq 0.08$ the quasi twodimensional degree of phonon spectrum becomes different (the spectrum becomes more "softer"). Another possible supposition is that, in $(BiI_3)_{(1-x)}(PbI_2)_x$ crystals with PbI_2 contents of $x = 0.2$ and $x = 0.3$, the interlayer accommodates one or more PbI_2 layers. This causes a change in the degree of quasi twodimensionality of the phonon spectrum and decrease in the frequency of interlayer vibrations and it manifests itself through a considerable change in the temperature coefficient value of the NQR frequency. At the same time, in the PbI_2 content range $0 < x \leq 0.08$, changes in $d\nu/dT$ are inconsiderable. It's possible to consider that PbI_2 nanoclusters are created in the content range $0 \leq x \leq 0.08$, which are located only within the layers of the crystal.

4. Conclusions

As a result, in crystals of alkali galogens $RbJO_3$ and $KBrO_3$ based on the study of temperature dependence of NQR frequencies we determined the frequencies of orientation and translational vibrations of alkaline halogens. In mixed semiconductor $(BiI_3)_{(1-x)}(PbI_2)_x$ we detected the anomally high absolute values of the temperature coefficients of the NQR frequency, which changes in the content PbI_2 of $0 \leq x \leq 0.08$ are insignificant. This indicates the conservation of the nature quazi twodimensional vibrational states for $x \leq 0.08$ PbI_2 $0 \leq x \leq 0.08$. The measurements of the temperature dependences of the spectrum parameters NQR at the PbI_2 content of $x \geq 0.20$, show that the synthesized crystals $(BiI_3)_{(1-x)}(PbI_2)_x$ compose glassy solid solution of the substitution type. PbI_2 groups (intercalants) are fully or partially ordered into PbI_2–BiI_3 semiconductor crystal system in this glassy solid. The PbI_2 groups can be located both within the crystalline layers

and between them. This lead to changes in the temperature coefficients of the frequency and to "softening" of the vibrational states of the changed quasi twodimensionality crystal structure.

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