CONCENTRATION DEPENDENCE OF ^{127}I NQR SPECTRUM PARAMETERS FOR MIXED LAYERED SEMICONDUCTORS $(\mathrm{BiI_3})_{1-x}(\mathrm{PbI_2})_x$

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The results of our studies dealing with the NQR spectra of ^{127}I in mixed layered semiconducting crystals $(\mathrm{BiI_3})_{1-x}(\mathrm{PbI_2})_x$ measured at a temperature of 77 K and in a wide range of $\mathrm{PbI_2}$ contents x $(0 < x < 0.5)$ are reported. In the range $0.05 < x < 0.2$, the observed behavior of ^{127}I NQR spectrum parameters testifies that $\mathrm{PbI_2}$ atomic groups are located within the structural layers of a $\mathrm{BiI_3}$ crystal. In this x-range, clusters composed of $\mathrm{PbI_2}$ groups were demonstrated to form an island structure. A further growth of the $\mathrm{PbI_2}$ content results in the appearance of a new ^{127}I NQR line which testifies that the mixed crystal $(\mathrm{BiI_3})_{1-x}(\mathrm{PbI_2})_x$ undergoes a structural phase transition at $x \approx 0.2$. A conclusion is made that, at $x \geq 0.2$, the synthesized crystal is a glassy substitutional solid solution, in which $\mathrm{PbI_2}$ atomic groups, being completely or partially ordered, are intercalated between the $\mathrm{BiI_3}$ crystal layers.

Layered semiconducting materials–such as $\mathrm{BiI_3}$, $\mathrm{CdI_2}$, $\mathrm{PbI_2}$–are known [1–3] to have anisotropic properties, which determines the use of those crystals as ionizing radiation detectors with a high energy resolution. First of all, it is a result of the existence of reversible structural variations (variations of anisotropic properties) that take place in the layered crystals under the action of ionizing radiation with various energies. In other words, the efficiency of the given materials is determined not only by their radiation stability, but also by a possibility to control their anisotropic properties, which allows layered semiconducting materials to be successfully applied in ionizing radiation detectors, as well as in optical and acoustic devices.

In this connection, the researches of the properties (the crystal parameters) of mixed crystals $(\mathrm{BiI_3})_{1-x}(\mathrm{PbI_2})_x$ and their dependences on the content and state of $\mathrm{PbI_2}$ atomic groups are challenging. The nuclear quadrupole resonance (NQR) spectra of ^{127}I nuclei in chemically pure $\mathrm{BiI_3}$ crystals $(x = 0)$ and in mixed layered crystals $\mathrm{PbI_2}$–$\mathrm{CdI_2}$ with isovalent iodine atoms were studied in works [4–7]. In this work, the NQR spectra of ^{127}I in mixed crystals $(\mathrm{BiI_3})_{1-x}(\mathrm{PbI_2})_x$ were studied for the first time. The spectra were measured at the temperature $T = 77$ K and in the frequency range $2-300$ MHz, by using an ISSh-2-13 quasicoherent NQR radio spectrometer. We also used a digital storage, which was necessary for the registration of weak and wide lines in the ^{127}I NQR spectrum.

The $(\mathrm{BiI_3})_{1-x}(\mathrm{PbI_2})_x$ crystals with the following $\mathrm{PbI_2}$ contents were studied: $x = 0$, 0.05, 0.08, 0.20, 0.30, 0.40, and 0.50. The measurements of NQR frequencies ν_1 and ν_2 for ^{127}I which correspond to the transitions $\pm 1/2 \leftrightarrow \pm 3/2$ and $\pm 3/2 \leftrightarrow \pm 5/2$, respectively, allowed us, on the basis of tables presented in work [8], to determine the dependences of the quadrupole interaction constant e^2Qq_{zz} and the asymmetry parameter $h = (q_{xx} - q_{yy})/q_{zz}$ of the electric-field-gradient tensor on the $\mathrm{PbI_2}$ content x. The determination accuracies for the asymmetry parameter $h(x)$ and the quadrupole interaction constant $e^2Qq_{zz}(x)$ depended on the NQR line widths and were not worse than ± 1.5 and $\pm 0.1\%$, respectively, of their absolute values.

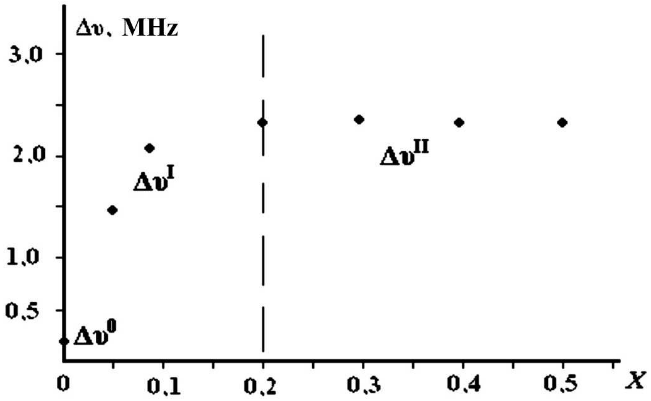
For a chemically pure crystal $\mathrm{BiI_3}$ $(x = 0)$ at $T = 77$ K, we obtained the frequencies $\nu_1^0 = 111.32$ MHz and $\nu_2^0 = 201.32$ MHz for two ^{127}I NQR transitions. Those frequencies correspond to the quadrupole interaction constant $e^2Qq_{zz}^0 = 682.18$ MHz and the asymmetry parameter of electric-field-gradient tensor $\eta^0 = 0.29 \pm 0.01$. The results obtained agree with those of work [7], which were obtained at studying a chemically pure $\mathrm{BiI_3}$ crystal.

As the $\mathrm{PbI_2}$ content x in the basic matrix of $\mathrm{BiI_3}$ crystal grows from 0.05 to 0.10, the quadrupole interaction constant $e^2Qq_{zz}^{\mathrm{I}}$ and the asymmetry parameter η^{I} of electric field gradient at ^{127}I nuclei change slightly (Table). The corresponding registered variations of the frequencies ν_1^{I} and ν_2^{I} do not exceed 3% of their absolute values (Table). At the same time, the linewidth $\Delta\nu^{\mathrm{I}}$ of the line at ν_1^{I} in the ^{127}I NQR spectrum changes by about an order of magnitude: from about 0.24 MHz at $x = 0$ to about 2.20 MHz at $x = 0.1$ (Figure). Note that the constant e^2Qq_{zz} is not changed, to within a measurement error, in the same interval of contents x. This can testify that, for the given PbI_2 content range ($0 \leq x \leq 0.10$), the introduction of PbI_2 atomic groups results in a minor modification of the layer symmetry and does not change the layered structure of the crystal. The symmetry C_{3i}^2 of layered crystals $(BiI_3)_{1-x}(PbI_2)_x$ in the range $0.01 \leq x \leq 0.10$ of PbI_2 contents can remain invariable. This assumption is based on the fact that the axes x and y of the components q_{xx} and q_{yy} of the electric-field-gradient tensor lie in the plane of crystal layers, whereas their axes z are perpendicular to the layers [4]. Therefore, when analyzing the ^{127}I NQR spectra, we can conclude that, in the range $0 < x < 0.10$ of PbI_2 contents, the layered structure of $(BiI_3)_{1-x}(PbI_2)_x$ crystals remains stable, and PbI_2 groups occupy places within the crystal layers to reduce their symmetry. In addition, PbI_2 groups can form layered clusters of the island type, the dimensions of which increase with the content x [5, 6].

We found a "new" line ν^{II} in the ^{127}I NQR spectrum of BiI_3 crystals with various PbI_2 contents (at $x = 0.20$, 0.30, 0.40, and 0.50) at $T = 77$ K. For instance, at $x = 0.20$, this line was characterized by the following parameters: $\nu_1^{\mathrm{II}} = 105.03$ MHz, $\nu_2^{\mathrm{II}} = 204.15$ MHz, $e^2Qq_{zz}^{\mathrm{II}} = 684.01$ MHz, and $\eta^{\mathrm{II}} = 0.15$. It is worth to note that the asymmetry parameter η^{II} for the new line ν^{II} in the ^{127}I NQR spectrum became approximately half as large: $\eta^{\mathrm{I}} = 0.29$ and $\eta^{\mathrm{II}} = 0.15$. At the same time, the constant e^2Qq_{zz} of the electric field gradient at ^{127}I nuclei was not changed considerably: $e^2Qq_{zz}^{\mathrm{I}} = 682.18$ MHz and $e^2Qq_{zz}^{\mathrm{II}} = 684.01$ MHz. This allowed us to draw conclusion that the growth of x was accompanied by an increase of the symmetry of the electric field gradient at ^{127}I nuclei.

In addition, when the PbI_2 content x in the BiI_3 crystal increased in the range $0.20 < x < 0.50$, the width $\Delta\nu^{\mathrm{II}}$ in the ^{127}I NQR spectrum practically was not changed ($\Delta\nu^{\mathrm{II}} \approx \Delta\nu^{\mathrm{I}}\big|_{x=10\%} \approx 2.30$ MHz). It is also significant that the line ν^{I} in the ^{127}I NQR spectrum with the parameters $e^2Qq_{zz}^{\mathrm{I}} = 682.18$ MHz and $\eta^{\mathrm{I}} = 0.29$ was not observed (or ceased to exist) in the content range $0.20 < x < 0.50$.

n	υ_1, MHz	υ_2, MHz	$\Delta\upsilon_1$, MHz	η	e^2Qq_{zz}, MHz	NQR spectrum interpretation
0	111.3	201.3	0.2	0.29	682.2	υ^0
0.05	111.4	201.3	1.5	0.29	682.8	υ^{I}
0.08	111.6	201.2	2.1	0.29	683	υ^1
0.20	104.3	204.2	2.3	0.15	684.0	υ^{II}
0.30	104.3	204.1	2.4	0.15	684.0	υ^{II}
0.40	104.3	204.1	2.3	0.15	684.0	υ^{II}
0.50	104.4	204.2	2.3	0.15	684.0	υ^{II}



Line widths $\Delta\nu$ of the ^{127}I NQR spectrum at 77 K (transition ±1/2 ↔ ±3/2) as a function of the PbI_2 atomic group content x in a mixed crystal $(BiI_3)_{1-x}(PbI_2)_x$ in two phases: I and II

It should be noted that the new line has no relation to the ^{127}I NQR line (transition ±1/2 ↔ ±3/2) of the pure PbI_2 crystal, because this crystal is characterized by lower values of ^{127}I NQR frequencies of two transitions at 77 K (4.36 and 8.95 MHz) [4, 9] in comparison with the corresponding frequencies observed by us (Table).

It is known [10] that, for chemically pure specimens with a high enough degree of crystal lattice perfection, the resonance line width in the NQR spectrum, $\Delta\nu$, must be, as a rule, very small in comparison with the frequency ν itself: $\Delta\nu/\nu \sim 10^{-3}$. Really, lattice distortions result in that the intermolecular distances r of the same type in the crystal are not accurately identical, i.e., a spread of distances r emerges. In turn, this can give rise to a certain divergence of values for the components of the electric-field-gradient tensor, Δq_{xx}, Δq_{yy}, and Δq_{zz}, as well as to an increase of the NQR spectrum line width $\Delta\nu$.

In work [10], it was also shown that, when the ratio $\Delta\nu/\nu$ ($\sim \Delta r/r$) increases to about 10^{-1}, the lines in the spectrum become unobservable. It is also known [10] that the product of the width and the intensity of an NQR line is proportional to the number of resonance nuclei that form this line. Therefore, the fact that the ^{127}I NQR line with the parameters $e^2Qq_{zz}^{\mathrm{I}} = 682.18$ MHz and $\eta^{\mathrm{I}} = 0.29$ was not observed in the content range $0.10 < x < 1$ can testify to a considerable reduction of the number of ^{127}I resonance nuclei which formed the line ν^{I}.

In the range $0.20 < x < 0.50$ of PbI_2 contents in the BiI_3 crystal, the width $\Delta\nu_1^{II}$ of the ^{127}I NQR spectrum practically did not vary. The ratio $\Delta\nu_1^{II}/\nu_1^{II}$ did not depend on the content x and equaled about 10^{-2}. This enabled us to conclude that the degree of lattice deformation did not change substantially in the range $0.20 < x < 0.50$ of PbI_2 contents in the BiI_3 crystal.

The analysis of the obtained experimental dependences of the asymmetry parameter ν_1^{II} and the width $\Delta\nu_1^{II}$ of line ν_1 on the PbI_2 content (Table) testifies that a structural phase transition may take place in the $(BiI_3)_{1-x}(PbI_2)_x$ crystal at the content $x \approx 0.20$. In this case, so that the total number of resonance ^{127}I nuclei in the $(BiI_3)_{1-x}(PbI_2)_x$ crystal at $x \geq 0.20$ has to be invariant, the new line ν^{II} in the ^{127}I NQR spectrum was formed at the expense of the line ν^{1}. In addition, the frequencies of ν^{1}- and ν^{II}-lines in the ^{127}I NQR spectrum demonstrated a stepwise change at $x \approx 0.20$ (Table).

Hence, the results obtained testify that, in the range $0.05 \geq x \geq 0.10$ of PbI_2 contents, island-like PbI_2 clusters which are located within the layers of the BiI_3 crystal can be formed in the structure of a mixed $(BiI_3)_{1-x}(PbI_2)_x$ crystal. In this case, the symmetry C_{3i}^2 of the BiI_3 crystal is not changed as a whole.

The analysis of NQR spectra testifies that, in the interval $x \geq 0.20$ of PbI_2 contents, the examined $(BiI_3)_{1-x}(PbI_2)_x$ crystal has properties of the solid substitution solution BiI_3–PbI_2. The so-called “new” $(BiI_3)_{1-x}(PbI_2)_x$ crystal can possess more isotropic glass-like properties. Since the NQR line width almost is not changed at $x \geq 0.20$, the “new” $(BiI_3)_{1-x}(PbI_2)_x$ crystal should have completely or partially ordered PbI_2 atomic groups which are located most probably in the intervals between the structural layers of the BiI_3 crystal. In this case, the general symmetry C_{3i}^2 of the BiI_3 crystal can be invariable.

At the content $x \approx 0.20$ of PbI_2 groups in the mixed $(BiI_3)_{1-x}(PbI_2)_x$ crystal, a phase transition can take place. This hypothesis is confirmed, e.g., by the disappearance of the line ν^{1} at low PbI_2 contents and the appearance of the line ν^{II} in the ^{127}I NQR spectrum at the PbI_2 group content $x \approx 0.20$. At $x \geq 0.20$, the virtual crystal $(BiI_3)_{1-x}(PbI_2)_x$ becomes mixed, for which the translational symmetry C_{3i}^2 can survive, nevertheless, as a whole.

Thus, a general conclusion can be drawn that, for mixed crystals $(BiI_3)_{1-x}(PbI_2)_x$, the transition from the anisotropic into the isotropic state can take place at reduced energies of ionizing radiation (i.e., the transition can enhance the sensitivity of those crystals to the energy of ionizing radiation).

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КОНЦЕНТРАЦІЙНА ЗАЛЕЖНІСТЬ ПАРАМЕТРІВ СПЕКТРА ЯКР ^{127}I ЗМІШАНИХ НАПІВПРОВІДНИКОВИХ ШАРУВАТИХ КРИСТАЛІВ $(BiI_3)_{(1-x)}(PbI_2)_x$

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Резюме

У роботі представлено результати досліджень спектрів ЯКР ^{127}I при 77 K напівпровідникових змішаних шаруватих кристалів $(BiI_3)_{(1-x)}(PbI_2)_x$ в широкому інтервалі $0 \leq x \leq 0,50$ вмісту PbI_2. Показано, що в діапазоні $0 \leq x \leq 0,20$ вмісту PbI_2 поведінка параметрів спектрів ЯКР ^{127}I при 77 K свідчить про знаходження груп PbI_2 в межах структурних шарів кристала BiI_3. При цьому вмісті PbI_2 у змішаному кристалі $(BiI_3)_{(1-x)}(PbI_2)_x$ відбувається утворення кластерів з груп атомів PbI_2 острівного типу. За подальшого збільшення вмісту PbI_2 у спектрі ЯКР ^{127}I кристала $(BiI_3)_{(1-x)}(PbI_2)_x$ з’являється нова лінія так, що у кристалі $(BiI_3)_{(1-x)}(PbI_2)_x$ при вмісті $(x \sim 0,20)$ PbI_2 відбувається структурний фазовий перехід. Стверджується, що синтезований новий кристал при $x > 0,20$ може бути твердим склоподібним розчином типу заміщення, в якому групи атомів PbI_2 – інтеркалянти повністю або частково впорядковані у проміжках між структурними шарами кристала BiI_3.