

Investigation of I^{127} NQR spectra of the mixed $(BiI_3)_{(1-n)}\cdot(PbI_2)_n$ semiconducting layered crystals

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The ^{127}I NQR spectra at 77 K of $(BiI_3)_{(1-n)}\cdot(PbI_2)_n$ semiconducting layered crystals in the wide concentration range $0 \le n \le 0.50$ at 0.10 steps have been studied. It has been shown that in the concentration range $0.05 \le n \le 0.10$, the $(BiI_3)_{(1-n)}\cdot(PbI_2)_n$ crystal exhibits the properties of a doped BiI_3 crystal containing intralayer PbI_2 clusters. In the $0.01 \le n \le 0.20$ range, the crystal shows the properties of an replacement type isotropic mixed crystal. At the PbI_2 impurity concentration $n \simeq 0.20$, the $(BiI_3)_{(1-n)}\cdot(PbI_2)_n$ crystal is subjected to so-called "concentration" phase transition and at $0.20 \le n \le 0.50$, a new $(BiI_3)_{(1-n)}\cdot(PbI_2)_n$ crystal exists including completely or partially ordered PbI_2 atomic groups.

Представлены результаты исследований спектров ЯКР ^{127}I при 77 К полупроводниковых смешанных слоистых кристаллов $(BiI_3)_{(1-n)}\cdot(PbI_2)_n$ в широком интервале концентраций $0 \le n \le 0.50$ с дискретностью 0.10. Показано, что в диапазоне концентраций $0.05 \le n \le 0.10$ кристалл $(BiI_3)_{(1-n)}\cdot(PbI_2)_n$ имеет свойства примесного кристалла BiI_3, содержащего внутрислоевые кластеры PbI_2. При $0.01 \le n \le 0.20$ кристалл $(BiI_3)_{(1-n)}\cdot(PbI_2)_n$ имеет свойства изотропного смешанного кристалла типа замещения. При концентрации $n \simeq 0.20$ примеси PbI_2 кристалл $(BiI_3)_{(1-n)}\cdot(PbI_2)_n$ испытывает концентрационный фазовый переход и при $0.20 \le n \le 0.50$ существует новый кристалл $(BiI_3)_{(1-n)}\cdot(PbI_2)_n$ с полностью или частично упорядоченными группами атомов PbI_2.

1. Introduction

It is known [1–3] that layered semiconducting materials BiI_3, CdI_2, PbI_2 have some properties [3, 4], which make it possible to use these crystals as X-ray detectors with high energy resolution properties. Besides, those crystals are used successfully in optical and acoustic devices because of their anisotropic properties. The efficiency of the materials being applied in X-ray detectors is defined by the presence of structural defects and impurities influencing the electron properties and defining the radiation resistance of the materials.

In this connection, of importance is to study the properties of $(BiI_3)_{(1-n)}\cdot(PbI_2)_n$ mixed crystals and to determine the concentration dependences of crystal parameters which may change depending on the impurity state. The nuclear quadrupole resonance spectra of ^{127}I nuclei (^{127}I NQR) in chemically pure BiI_3 crystals ($n = 0$) and in the $PbI_2\cdot CdI_2$ mixed layered crystals containing isovalent iodine atoms were studied in [5, 6]. The ^{127}I NQR spectra of the $(BiI_3)_{(1-n)}\cdot(PbI_2)_n$ mixed crystals are studied in this work for the first time.

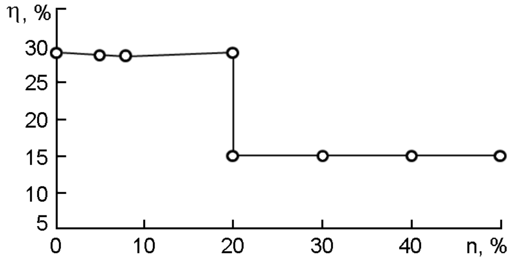

Fig. 1. Concentration dependence of the tensor asymmetry parameter η of electrical field gradient.

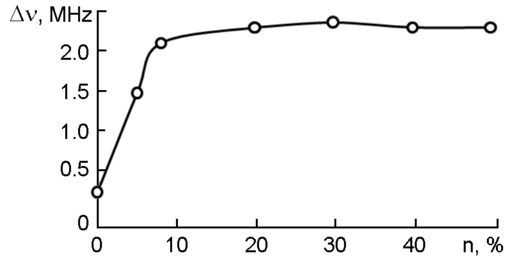

Fig. 2. Concentration dependence of the width of ^{127}I NQR spectrum line corresponding to transition ±1/2↔±3/2.

2. Experimental

The ^{127}I NQR spectra of the $(BiI_3)_{(1-n)}\cdot(PbI_2)_n$ crystals under study at temperature T = 77 K in the frequency range 2–300 MHz were measured using a quasi-coherent NQR spectrometer ISSh-2-13. A digital accumulator for registration of weak and wide lines in the NQR spectra was used, too. The BiI_3 crystals with different concentrations n of PbI_2 impurity were investigated (n = 0, 0.05, 0.10, 0.20, 0.30, 0.40 and 0.50). The measured frequency values υ_1 and υ_2 of the ^{127}I NQR corresponding to transitions ±1/2↔±3/2 and ±3/2↔±5/2, provided, proceeding from the tabular data [7], determination of the concentration dependences of the quadrupole coupling constant $e^2Qq_{zz}(n)$ and asymmetry parameter $\eta(n)$ of the electric field gradient tensor ($\eta = (q_{xx} - q_{yy})/q_{zz}$) on ^{127}I nuclear resonance. The NQR data are presented in Table. The determination accuracy of the asymmetry parameter and quadrupole coupling constant were defined by the line width and did not exceed ±1.5 % and ±0.1 % of absolute values thereof.

3. Results and discussion

It was found that for chemically pure BiI_3 crystal (n = 0) at 77 K, the ^{127}I NQR frequencies $\upsilon_1{}^0$ and $\upsilon_2{}^0$ corresponding to two transitions make 111.320 and (201.380±0.010) MHz, respectively. The presented frequencies $\upsilon_1{}^0$ and $\upsilon_2{}^0$ correspond to the quadrupole coupling constant $e^2Qq_{zz}{}^0$ = (682.18±0.01) MHz and the tensor asymmetry parameter η^0 = 0.29±0.1. The results obtained agree with experimental data [5].

It is to note that the constant $e^2Qq_{zz}{}^{I}$ and asymmetry parameter η^{I} change insignificantly, when concentration value n of PbI_2 impurity in the basic BiI_3 matrix increases from 0.05 to 0.10 (Fig. 1). The observed changes for the frequencies $\upsilon_1{}^{I}$ and $\upsilon_2{}^{I}$ do not exceed 10 % of their absolute values (Table). While the width $\Delta\upsilon^{I}$ of the υ_1 line in the ^{127}I NQR spectrum changes by one decimal order in the same concentration n interval: $\Delta\upsilon^1|_{n=0}$ ~ 0.24, $\Delta\upsilon^1|_{n=0.10}$ ~ 2.20 MHz (Fig. 2). These experimental data evidence that in concentration range $0 \le n \le 0.10$, the reduction of intralayer sym-

Table.

n	υ_1, MHz	υ_2, MHz	$\Delta\upsilon_1$, MHz	η	e^2Qq_{zz}, MHz	Interpretation NQR Spectra
0	111.32	201.38	0.21	0.29	682.18	υ^0
0.05	111.4	201.3	1.46	0.287	682.75	υ^{I}
0.08	111.601	201.2	2.1	0.285	682.97	υ^1
0.20	111.4	201.2	2.3	0.29	682.2	υ^{I}
0.20	104.35	204.2	2.3	0.15	684.01	υ^{II}
0.30	104.325	204.1	2.36	0.15	684.005	υ^{II}
0.40	104.3	204.15	2.3	0.15	684.02	υ^{II}
0.50	104.35	204.17	2.3	0.15	684.025	υ^{II}

metry is insignificant while the interlayer symmetry does not change. The C_{3i}^2 symmetry for crystal $(BiI_3)_{(1-n)}\cdot(PbI_2)_n$ in the concentration range $0 \le n \le 0.10$ does not change as a whole. This assumption is based on the fact that x and y axes of q_{xx} and q_{yy} components of the electrical field gradient tensor lie in the plane of crystal layers and axes z are perpendicular to the layers [5]. Therefore, the layered structure of $(BiI_3)_{(1-n)}\cdot(PbI_2)_n$ crystals can be supposed to be maintained for the concentration range $0 < n < 0.10$ with impurity groups PbI_2 being situated within the crystal layers. Moreover, PbI_2 groups may form interlayer clusters of "island" type with dimensions increasing with the increase of concentration n.

For the BiI_3 crystals with the concentration n of PbI2 impurity 0.20, 0.30, 0.40 and 0.50, we have revealed a new line υ^{II} in the ^{127}I NQR spectrum at 77 K. So, for $n = 0.20$, the line υ^{II} at 77 K is characterized by the following parameters: $\upsilon_1^{II} = 105.027$, $\upsilon_2^{II} = 204.150$ MHz, $e^2Qq_{zz}^{II} = 684.01$ MHz, $\eta^{II} = 0.15$. It is important to note that for this new line of NQR spectrum of ^{127}I, the asymmetry parameter η^{II} becomes approximately halved: $\eta^I = 0.29$ and $\eta^{II} = 0.15$. Thus, the constant e^2Qq_z of the electric field gradient on ^{127}I nuclei does not change considerably: $e^2Qq_{zz}^I = 682.18$ and $e^2Qq_{zz}^{II} = 684.01$ MHz. This allows to conclude that with growing n, the crystal interlayer symmetry increases.

In addition, at increasing concentration n of PbI_2 impurity in the interval $0.20 < n < 0.50$, the width $\Delta\upsilon^{II}$ of the new υ^{II} line in the ^{127}I NQR spectrum remains essentially unchanged ($\Delta\upsilon^{II} \sim \Delta\upsilon^I|_{n=10\%} \sim 2.30$ MHz). It is also of interest that the line υ^I in the ^{127}I NQR spectrum with the parameters $e^2Qq_{zz}^I = 682.18$ MHz and $\eta^I = 0.29$ in the n $0.10 < n < 0.50$ range is not observed. It is known [7] that for the chemically pure samples with a rather high perfection of crystal lattice, the width of resonance line $\Delta\upsilon$ of the NQR spectrum must as a rule be very small as compared to frequency υ of the NQR line: $\Delta\upsilon/\upsilon \sim 10^{-3}$. Indeed, the presence of distortions in the lattice results in that the intermolecular distances r of the same type in the crystal are not strictly identical. There appears some variation Δr of r distances. This may, in turn, cause some variation of the field tensor components Δq_{xx}, Δq_{yy} and Δq_{zz} of the electric field gradient q_{zz} and increasing width $\Delta\upsilon_1^{II}$ of NQR spectrum line. It was also shown in [7] that for $\Delta\upsilon/\upsilon \sim \Delta r/r \sim 10^{-1}$, the nuclear quadrupole resonance signals become unobservable.

It is known [7] also that the product of width and intensity of NQR line is proportional to the number of resonant nuclei which form this line. Therefore, the fact that in the concentration range $0.10 < n < 0.50$, the line υ^1 of ^{127}I NQR spectrum with the parameters $e^2Qq_{zz}^I = 682.18$ MHz and $\eta^I = 0.29$ becomes unobserved, can testify about considerable reduction of number of ^{127}I resonant nuclei which form the line υ^1. We have found that in the interval of PbI_2 impurity concentrations $0.20 < n < 0.50$ in the BiI_3 crystal, the width $\Delta\upsilon_1^{II}$ of the line υ_1^{II} in ^{127}I NQR spectrum does not change essentially. The ratio $\Delta\upsilon_1^{II}/\upsilon_1^{II}$ is independent of the concentration n and makes $\sim 10^{-2}$. This enables to record the rather wide lines υ_1^{II} of ^{127}I NQR spectrum in the concentration range $0.20 < n < 0.50$.

Analysis of the obtained experimental concentration dependences both of the asymmetry parameter and of the υ_1 line width (Figs. 1 and 2) indicates that at the concentration $n \sim 0.20$, the so-called "concentration" phase transition occurs in the $(BiI_3)_{(1-n)}\cdot(PbI_2)_n$ crystal. Taking into account that the total number of resonant ^{127}I nuclei in the $(BiI_3)_{(1-n)}\cdot(PbI_2)_n$ crystal should be constant, the new line υ^{II} in the ^{127}I NQR spectrum at $n \ge 0.20$ is formed at the expense of resonant nuclei forming the line υ^I. In addition, at $n \sim 0.20$, the concentration dependences of frequencies υ_1 and υ_2 show a jump (Table).

4. Conclusions

Thus the results obtained show that in the concentration range $0.05 \ge n \ge 0.10$, PbI_2 impurity islands or clusters can be formed in the $(BiI_3)_{(1-n)}\cdot(PbI_2)_n$ structure which are disposed within BiI_3 crystal layers. The symmetry of impurity BiI_3 crystal as a whole does not change. It is shown that in the concentration range $0.10 \ge n \ge 0.20$, the $(BiI_3)_{(1-n)}\cdot(PbI_2)_n$ crystal under study exhibits the properties of $BiI_3\cdot PbI_2$ solid solution of substitution type. The appearing virtual crystal $BiI_3\cdot PbI_2$ is characterized by isotropic glassy properties. As a result, due to distortion of transmission symmetry of the isotropic mixed crystal $BiI_3\cdot PbI_2$, the ^{127}I

NQR spectrum is not observed. At the concentration value $n \sim 0.20$, the mixed $(BiI_3)_{(1-n)} \cdot (PbI_2)_n$ crystal undergoes a concentration phase transition. An evidence thereof is, for example, the disappearance of low-concentration υ^{I} line and appearance of a new high-concentration υ^{II} one in the ^{127}I NQR spectrum. In this case, the impurity crystal $(BiI_3)_{(1-n)} \cdot (PbI_2)_n$ (at $n \geq 0.20$) changes into the mixed crystal $(BiI_3)_{(1-n)} \cdot (PbI_2)_n$, where the translational symmetry of crystal as a whole can be retained.

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Дослідження спектрів ЯКР ^{127}I змішаних шаруватих напівпровідникових кристалів $(BiI_3)_{(1-n)} \cdot (PbI_2)_n$

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Досліджено спектри ЯКР ^{127}I при 77 К напівпровідникових змішаних шаруватих кристалів $(BiI_3)_{(1-n)} \cdot (PbI_2)_n$ у широкому інтервалі концентрацій $0 \leq n \leq 0.50$ з дискретністю 0.10. Показано, що у діапазоні концентрацій від $0.05 \leq n \leq 0.10$ кристал $(BiI_3)_{(1-n)} \cdot (PbI_2)_n$ має властивості домішкового кристала BiI_3 з внутрішньошаруватими кластерами PbI_2. При $0.01 \leq n \leq 0.20$ кристал $(BiI_3)_{(1-n)} \cdot (PbI_2)_n$ має властивості ізотропного змішаного кристала типу заміщення. При $n \simeq 0.20$ домішки PbI_2 у кристалі $(BiI_3)_{(1-n)} \cdot (PbI_2)_n$ відбувається концентраційний фазовий перехід і при $0.20 \leq n \leq 0.50$ утворюється новий кристал $(BiI_3)_{(1-n)} \cdot (PbI_2)_n$ з повністю або частково впорядкованими групами атомів PbI_2.