Semiconductor Physics, Quantum Electronics & Optoelectronics, 2017. V. 20, N 3. P. 340-343.
doi: https://doi.org/10.15407/spqeo20.03.340

PACS 76.60.Gv

I^{127} NQR spectra of $Pb_{1-x}Cd_xI_2$ and $(BiI_3)_{(1-x)}(PbI_2)_x$ of mixed layered semiconductors

I.G. Vertegel[1], E.D. Chesnokov[1], O.I. Ovcharenko[1], L.S. Ivanova[1], Yu.P. Gnatenko[1], I.I. Vertegel[2]
[1]*Institute of Physics, NAS of Ukraine,*
46, prospect Nauky, 03680 Kyiv, Ukraine
[2]*National Technical University "KPI",*
37, prospect Peremohy, 03056 Kyiv, Ukraine

Abstract. The results of studying the concentration and temperature dependences of NQR spectrum parameters inherent to I^{127} in mixed layered semiconductors $Pb_{x-1}Cd_xI_2$ and $(BiI_3)_{(1-x)}(PbI_2)_x$ are presented for $x \le 0.30$ and $T = 77…150$ K. It has been shown that, for the low content $x \le 0.08$ PbI_2 for $(BiI_3)_{(1-x)}(PbI_2)_x$ and $x \le 0.02$ CdI_2 for $Pb_{1-x}Cd_xI_2$, the temperature coefficients of NQR frequency don't undergo significant changes, which is indicative of conservation of the quasi-two-dimensional nature of the vibration states. The possibility to form nanoclusters of PbI_2 and CdI_2 as well as their influence on the parameters of the NQR spectra has been discussed.

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

Manuscript received 18.05.17; revised version received 10.07.17; accepted for publication 06.09.17; published online 09.10.17.

1. Introduction

In this work, the temperature dependences of parameters inherent to NQR spectra of the layered semiconductor crystals $(BiI_3)_{(1-x)}(PbI_2)_x$ and $Pb_{1-x}Cd_xI_2$ have been studied. The temperature coefficients of the NQR spectrum parameters are highly sensitive to changes in the crystal dynamic parameters (amplitudes, frequencies) [1, 2]. The urgency of studies of solid solutions of layered semiconductor crystals $(BiI_3)_{(1-x)}(PbI_2)_x$ and $Pb_{1-x}Cd_xI_2$ is first of all associated with the possibility of formation of cluster structures in these crystals, which significantly affects their properties. Recently, the interest significantly increased in finding of semiconductor materials that are suitable for development on their base the detectors with high radiation energy distribution, which can operate at room temperature. The promising materials are those that have a layered structure with relatively high atomic number of components. The absorption and reflectance spectra as well as X-ray structural analysis of $(BiI_3)_{1-x}(PbI_2)_x$ mixed crystals, photoluminescence spectra were studied in [3, 4]. The I^{127} nuclear quadrupole resonance (NQR) spectra of chemically pure BiI_3 crystals and mixed layered semiconductor were studied in [5-8].

At the same time, NQR investigations are of episodic character and don't completely explain the dynamic character of these crystals. In this work, for the first time, the authors fulfilled studying the temperature dependence of NQR frequencies in crystals under consideration.

2. Experimental

The I^{127} NQR spectra of the crystals under investigation were measured within the temperature range 77 to 150 K and the frequency range 5…300 MHz by using quasi-coherent NQR spectrometer. Accuracy was determined by the half-width of the NQR lines, and for the crystals $(BiI_3)_{(1-x)}(PbI_2)_x$ and $Pb_{1-x}Cd_xI_2$, it was limited by the interval ±100 kHz. Crystals with PbI_2 contents of $x =$ 0.0, 0.05, 0.08, 0.2, 0.3 and CdI_2: $x = 0$, 0.02, 0.1 were studied. Measurements of the I^{127} NQR frequencies ν corresponding to the $\pm1/2 \leftrightarrow \pm3/2$ and $\pm5/2 \leftrightarrow \pm3/2$

transitions enabled to determine the temperature and concentration dependences of the quadrupole interaction constans $e^2Qq_{zz}(x)$ and the asymmetry parameter $\eta(x)$ of the electric-field-gradient tensor $\eta = (q_{xx} - q_{yy})/q_{zz}$ ($\eta = (q_{xx}-q_{yy})/q_{zz}$) (EFGT). The accuracy of determination of the asymmetry parameter and quadrupole interaction constant depended on the line width and was no worse than ±1.5% and ±0.1% of their absolute values, respectively. At temperatures above the Debye one, T_D, the NQR frequency usually exhibits a linear dependence [1]. When studying the temperature dependence of the NQR frequencies of the lines within the temperature range 77 to 150 K, it was found that the NQR frequency of those lines varied linearly with temperature. The experimental results obtained for the NQR lines ν made it possible to determine the temperature coefficients of the NQR spectrum parameters: $k_1 = d\nu/dT$ (±1/2↔±3/2), $k_2 = d\nu/dT$ (±3/2↔±5/2). The accuracy of determination of the specified parameters was defined by the width of the NQR lines and precision of sample temperature stabilization and was no worse than ±10% for all lines. The data of our measurements are summarized in Table.

3. Experimental results and discussion

With increasing the PbI_2 content in the crystal $(BiI_3)_{(1-x)}(PbI_2)_x$ and CdI_2 in $Pb_{1-x}Cd_xI_2$, the line width of the NQR I^{127} (±3/2↔±5/2) is significantly increased. With increasing PbI_2 and CdI_2 content x in the crystals under investigation from 0 up to 0.30, the width Δν of lines ν of I^{127} NQR in the same range of content x varies by about an order of magnitude: $\Delta\nu|_{x=0} \sim 0.24$, $\Delta\nu|_{x=0.3} \sim 2{,}30$ MHz, $\Delta\nu_1|_{x=0} \sim 0.2$, $\Delta\nu_1|_{x=0.1} \sim 1.40$ MHz. It must be noted that the value of the constants e^2Qq_{zz} in the crystal $(BiI_3)_{(1-x)}(PbI_2)_x$ in the range of content x ($0 \le x \le 0.10$) does not change within the measurement error [5]. For crystals PbI_2 at $T = 77$ K, it was revealed that the value of e^2Qq_{zz} is 29.83 MHz, and the asymmetry parameter of the (EFGT) is equal to zero. The quadrupole constant of interaction is 30.708 MHz for solid solutions $Pb_{1-x}Cd_xI_2$ ($x = 0.02$), and the asymmetry parameter EFGT is equal to 14%. In this case, the ratio of NQR line width to the NQR frequency is 0.052. Proceeding from the obtained results, it can be considered that there is violation of axial symmetry of electric field gradient at the resonant nuclei I^{127} during formation of solid solutions with a low content of Cd component. This may be due to the fact that the introduction of Cd atoms in the matrix PbI_2 leads to minor violation of internally layer anisotropy due to the fact that ionic radius Pb^{2+} and Cd^{2+} are significantly different (1.21 and 0.97Å, respectively). This leads to emergence of internal layer mechanical stresses of crystalline lattice, and, as consequence, to the decrease in the axial symmetry of the electric field gradient along the axes q_{xx} and q_{yy} that are inside the crystal layer.

Thus, for the range of content $0 \le x \le 0.1$, introduction of groups of atoms PbI_2 and CdI_2 causes the minor change of symmetry of layers and does not change the layered structure of crystals. For that, the symmetry of studied layered crystals in the range of content $0 \le x \le 0.1$ can remain unchanged C_{3i}^2. This assumption is based on the fact that the x and y axes of components q_{xx} and q_{yy} of the electric field gradient tensor lie in the plane of the crystal layers and z-axis are perpendicular to the layers [6]. Therefore, when analyzing the NQR I^{127} spectra, it can be concluded that in the interval of PbI_2 and CdI_2 content $0 < x < 0.1$ layered structure of crystals $(BiI_3)_{(1-x)}\cdot(PbI_2)_x$ and $Pb_{x-1}Cd_xI_2$ is remained and PbI_2 and CdI_2 groups are located within the crystal layers. In addition, the PbI_2 and CdI_2 groups may form the layer clusters of island type, the size of which increases with increasing the content x [8, 9]. A further growth of cadmium component content in crystals $Pb_{1-x}Cd_xI_2$ up to $x \ge 0.1$ causes a significant broadening of NQR line. The relative broadening of NQR line is 0.33, the quadrupole interaction constant increases up to 43.429 MHz, and parameter EFGT – to 63%.

It should be also noted that the shape of NQR lines for crystals $Pb_{0.9}Cd_{0.1}I_2$ at $T = 77$ K is complex and includes a number of vague lines [10]. Existence of this structure in the NQR lines may indicate formation of an "island" (heterophase) structure.

It is known that for the chemically pure samples with sufficiently high degree of perfection of the crystal lattice, as a rule, the width of the NQR spectra line Δν must be very small in comparison with the NQR line frequency $\Delta\nu/\nu \sim 10^{-3}$ [11]. It is known that for the chemically pure samples with sufficiently high degree of perfection of the crystal lattice as a rule the width of the NQR spectra line Δν must be very small in comparison with the NQR line frequency $\Delta\nu/\nu \sim 10^{-3}$ [11]. 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 it lead to certain divergence of values for the components of the electric-field-gradient tensor, Δq_{xx}, Δq_{yy} and Δq_{zz} and to increasing the NQR spectrum line width Δν. In the work [11], it was also shown that the ratio Δν/ν ($\sim \Delta r/r$) increases to about 10^{-1}, and lines of the spectrum become unobservable. It is also known [1] that the product of the width and the intensity of the NQR line is proportional to the number of resonance nuclei that form this line. Therefore, the fact that, in the range of content CdI_2 $0.1 < x < 1$ in crystals $Pb_{1-x}Cd_xI_2$ and in the range of content PbI_2 $x \ge 0.2$ in crystals $(BiI_3)_{(1-x)}(PbI_2)_x$ the line ν with the parameters $e^2Qq_{zz} = 682.18$ MHz and $\eta = 0.29$ was not observed, can testify to a considerable reduction of the number of I^{127} resonance nuclei that are responsible for this line. It was received [5] that for chemically pure crystal BiI_3 ($x = 0$) at 77 K I^{127} NQR frequencies of two transitions $\nu_{(1/2\leftrightarrow\pm3/2)}$ and $\nu_{(\pm3/2\leftrightarrow\pm5/2)}$ are accordingly equal to 111.320 and 210.380 MHz. The constant of the quadrupole interaction $e^2Qq_{zz} =$

682.18 MHz and asymmetry parameter of the electrical field gradient tensor $\eta = 0.29 \pm 0.01$ correspond to given values of frequencies at 77 K.

For BiI_3 crystals at 77 K with PbI_2 contents $x = 0.20$ and 0.3, the line ν' was observed in the I^{127} NQR spectrum, the parameters of which differed significantly from the parameters of the I^{127} line ν for pure BiI_3 (Figure) [5]. For example, at $x = 0.2$, the ν' line at 77 K is characterized by the following values of parameters: $\nu_{(\pm1/2\leftrightarrow\pm3/2)} = 104.35$ MHz, $\nu_{(\pm5/2\leftrightarrow\pm3/2)} = 204.20$ 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 I^{127} NQR spectrum is decreased about twice: from $\eta = 0.29$ down to $\eta' = 0.15$. The value of the constant e^2Qq_{zz}' of the electric field gradient at the I^{127} 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, symmetry of the electric field gradient increases.

It is known that for an intracrystalline field with the asymmetry parameter $\eta = 0$ [1]

$$\nu_{\left|\pm\frac{5}{2}\right|\leftrightarrow\left|\pm\frac{3}{2}\right|} = \left|\frac{3e\overline{Qq_{zz}}}{hI(2I-1)}\right|,$$

where Q is the nuclear quadrupole moment, e – electron charge, I – the nucleus spin, $\overline{q_{zz}}$ – time-averaged EFGT, averaged by lattice vibrations. Note that q_{zz} is defined by contributions from the covalent bonds of the ion and from the point charges of the lattice ions q^i_{zz} [12]. It was shown [2, 13] that the temperature dependence of the NQR frequency in the case of zero EFGT asymmetry parameter and if q^i_{zz} contribution from the point charges can be neglected and this may be used to interpret long wave low-frequency phonon spectra of crystals. The vibrations with frequencies not exceeding 200 cm^{-1} are the most efficient in averaging q_{zz}.

For layered semiconductor crystals, the contribution of lattice point charges to temperature dependence of the NQR frequencies can be significant [14], which leads to inability of using the dual frequency model for averaging GEF. If symmetry of EFGT differs from the axial one (for BiI_3, crystal, $\eta = 29\%$) for the spin $I = 5/2$, the NQR frequency, eQq_{zz}, and η are related by the solutions of the corresponding secular equations [15]. The absolute values of the temperature coefficients of the NQR frequencies in crystals of alkaline halogens are mainly due to fluctuations of isolated alkaline halogens; while in layered crystals – by 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 lead to the vibrational states of quasi-two-dimensional character [6]. The vibrations that can efficiently average the electric field gradient in the studied crystals primarily include low-frequency interlayer vibration associated with the weak interaction between the layers. The temperature coefficients of the frequency (k_1 and k_2) in $(BiI_3)_{1-x}(PbI_2)_x$ 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 $0 \le x \le 0.08$ remain constant. It suggests that, at these x values, the low-frequency interlayer vibrations undergo no significant changes and that the inclusion of PbI_2 groups does not lead to the significant change in the degree of two-dimensionality of the crystal structure.

The temperature coefficients of the frequency ($d\nu/dT$) increased in comparison with the line ν' (table) for this new line ν in the NQR spectrum. For example, for the line ν' at $x = 0.3$ $d\nu/dT = -74.6$ kHz/K, whereas for the line ν at $x = 0$ $d\nu/dT = -15.3$ kHz/K. As a result, one can made the conclusion that, at the PbI_2 content range $0.2 \le x \le 0.6$ as compared with range $0 \le x \le 0.08$, the degree of quasi-two-dimensionality of phonon spectra becomes different (spectrum becomes 'softer'). Another possible assumption 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 spacing accommodates one or more PbI_2 layers. It causes a change in the degree of quasi-two-dimensionality of the phonon spectrum and a decrease in the frequency of interlayer vibrations, which manifests itself through a considerable change in the value of temperature coefficient of the NQR frequency. At the same time, for the PbI_2 content range $0 < x \le 0.08$, changes in $d\nu/dT$ are insignificant. It's possible to state that PbI_2 nanoclusters are created within the content range $0 \le x \le 0.08$, when they are located only within the layers of the crystal.

Crystals	k_1/ν_1 ($10^{-3}K^{-1}$) ±1/2↔±3/2	k_2/ν_2 ($10^{-3}K^{-1}$) ±3/2↔±5/2	η	Spectral lines
BiI_3	–0.1402	–0.0819	0.29	ν
$(BiI_3)_{0.95}(PbI_2)_{0.05}$	–0.1543	–0.090	0.287	ν
$(BiI_3)_{0.92}(PbI_2)_{0.08}$	–0.1316	–0.089	0.285	ν
$(BiI_3)_{0.8}(PbI_2)_{0.2}$	*	–0.1523	0.15	ν'
$(BiI_3)_{0.7}(PbI_2)_{0.3}$	*	–0.1754	0.15	ν'
PbI_2	*	–0.030	0.00	ν_1
$Pb_{0.98}Cd_{0.02}I_2$	*	–0.032	0.014	ν_1

* The temperature dependence was not investigated.

4. Conclusions

In the mixed layered semiconductors $(BiI_3)_{(1-x)}(PbI_2)_x$ and $Pb_{1-x}Cd_xI_2$, the values of the temperature coefficients of the NQR frequency has been defined, which changes within the content range of PbI_2 $0 \le x \le 0.08$ and CdI_2 $x \ge 0.2$ are insignificant, indicating conservation of nature of quasi-two-dimensional vibrational states for $x \le 0.08$ in the case of PbI_2 and $x \le 0.08$ – of CdI_2 The measurements of the temperature dependences of the NQR spectrum parameters at the PbI_2 content $x > 0.2$ and that for CdI_2 $x > 0.1$ show that the synthesized crystals $(BiI_3)_{(1-x)}(PbI_2)_x$ and $Pb_{1-x}Cd_xI_2$ are glassy solid solutions of the substitution type. At this, the synthesized PbI_2 and CdI_2 groups (intercalates) are fully or partially ordered into the semiconductor crystal system. It leads to changes in the temperature coefficients of the frequency and 'softening' the vibrational states, which causes changing the quasi-two-dimensionality of the crystal structure.

References

1. Semin G.K., Babushkina T.A., and Yakobson G.G. *Nuclear Quadrupole Resonance in Chemistry*. New York, Wiley, 1975.
2. Baisa D.F., Barabash A.I., Puchkovskaya G.A. Assignment of lattice vibrations of lithium jodate from IR, Raman and NQR data. *Phys. Lett.* 1973. **43A**. P. 453–454.
3. Furyer M.S., Skubenko P.A., Bukivskij P.M. et al. Study of the photoluminescence and properties of $Pb_{x-1}Cd_xI_2$ alloys. *J. Appl. Phys*. 2010. **108**, No. 10. P.103711-1–103711-5.
4. Gorban I.S., Donets V.V., Rudko S.V., Sushkevich T.N. Optical properties of $(BiI_3)_{(1-x)}(PbI_2)_x$ crystals. Ukr. Fiz. Zh. 1981. **26**, No. 3. P. 495–497 (in Russian).
5. Barabash A.I., Vertegel I.G., Chesnokov E.D., Ovcharenko A.I., Gnatenko Yu.P. Concentration dependence of ^{127}I NQR spectrum parameters for mixed layered semiconductors $(BiI_3)_{(1-x)}(PbI_2)_x$. *Ukr. J. Phys.* 2011. **56**, No. 2. P. 158–160.
6. Lyfar D.L. and Ryabchenko S.M. Effect of aniline intercalation on the temperature behaviour in PbI_2. *Zhurnal fiziki nizkikh temperatur.* 1979. **5**, No. 7. P. 779–782 (in Russian).
7. Konopleva K.G., Venskovskij N.U., Tupoleva A.L., Babuchkina T.A. Spektru NQR I^{127} stroenie nekotorich iodidov kadmij I svinza sintezirovanich raslichnumi metodami. *Koordinatsionnaia khimiya*. 1999. **23**, No. 7. P. 505–509 (in Russian).
8. Gnatenko Yu.P., Barabash A.I., Vertegel I.G., Chesnokov E.D., Ovcharenko A.I., Pogrebnyak S.V. Investigation of NQR I^{127} spectra of the $(BiI_3)_{(1-x)}(PbI_2)_x$ semiconducting layered crystals. *Functional Materials.* 2010. **17**, No. 1. P. 37–42.
9. Bukivskii A.P., Gnatenko Yu.P., Piryatinskii Yu.P., Gamernyket R.V. Nature of radiative recombination processes in layered semiconductor $Pb_{x-1}Cd_xI_2$ nanostructural scintillation material. *J. Lumin.* 2017. **185**. P. 83–91.
10. Gnatenko Yu.P., Beinik I.A., Barabash A.I., Vertegel I.G., Chesnokov E.D., Ovcharenko A.I., Ivanova L.S. NQR investigation of crystal structure peculiarities of layered $Pb_{x-1}Cd_xI_2$ semiconductors. *Functional Materials.* 2008. **15**, No. 2. P. 19–21.
11. Fedin E.I. and Kitaigorodsii A.I. The investigation of some organic solutions compound by NQR method. *Kristallografiya*. 1961. **6**, No. 3. P. 406–415 (in Russian).
12. Lyfar D.L., Goncharuk V.E., Ryabchenko S.M. Temperature dependence of nuclear quadrupole resonance in layer-type crystals. *phys. status solidi* (*b*). 1976. **76**. P. 183–189.
13. Baisa D.F., Barabash A.I., Vertegel I.G. The temperature dependence of the NQR frequencies and interpretation long-wave spectrum of alkaline halogen hexagonal modification. *Izvestiya AN SSSR. Ser. Fiz.* 1978. **51**, No. 10. P. 2110–2115 (in Russian).
14. Lyfar D.L. and Ryabchenko S.M. Effect of piperidin intercalation on nuclear quadrupole resonance the in PbI_2. *Zhurnal fiziki nizkikh temperatur.* 1979. 3, No. 10. P. 1297–1301 (in Russian).
15. Semin G.K. On solving secular equations for half-integer spins (J = 5/2, 7/2, and 9/2). *Russian Journal of Physical Chemistry*. 2007. **81**, No. 1. P. 38–46.