

# Influence of $\text{Mn}^{2+}$ ions on parameters of the $^{127}\text{I}$ NQR spectrum of a mixed layered $\text{Pb}_{1-x}\text{Mn}_x\text{I}_2$ semiconductor

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The concentration dependences of the parameters of the  $^{127}\text{I}$  NQR spectrum for  $\text{Pb}_{1-x}\text{Mn}_x\text{I}_2$  mixed layered semiconductors have been investigated. It was shown that in the range of  $0.00 < x \leq 0.1$ ,  $\text{Mn}^{2+}$  ions mainly replace  $\text{Pb}^{2+}$  ions in the crystalline layers. It is possible to form nanocluster domains in  $\text{Pb}_{1-x}\text{Mn}_x\text{I}_2$  crystals. It is shown that the nanocluster domain  $\text{Pb}_{1-x}\text{Mn}_x\text{I}_2$  structure leads to the change of the NQR spin echo signals integral intensity. The decrease of the spin lattice relaxation time which has been revealed indicates the existence of the additional mechanism of the  $^{127}\text{I}$  NQR relaxation. This mechanism is connected with the dipole interaction of the  $\text{Mn}^{2+}$  ions with the nearest  $^{127}\text{I}$  nuclei.

**Keywords:** nuclear quadrupole resonance, layered semiconductors, nanoclusters.

Приведены результаты исследований концентрационных зависимостей параметров спектра ЯКР  $^{127}\text{I}$  смешанных слоистых полупроводников  $\text{Pb}_{1-x}\text{Mn}_x\text{I}_2$ . Показано, что в интервале содержания  $\text{MnI}_2$   $0.00 < x \leq 0.1$  ионы  $\text{Mn}^{2+}$  в основном замещают ионы  $\text{Pb}^{2+}$  в кристаллических слоях, а нанокластерная доменная структура  $\text{Pb}_{1-x}\text{Mn}_x\text{I}_2$  приводит к изменению интегральной интенсивности спиновых эхосигналов ЯКР. Обнаруженное сокращение времени спин-решеточной квадрупольной релаксации ядер  $^{127}\text{I}$  указывает на существование дополнительного механизма релаксации. Этот механизм связан с дипольным взаимодействием  $\text{Mn}^{2+}$  с ближайшими ядрами  $^{127}\text{I}$ .

**Вплив іонів  $\text{Mn}^{2+}$  на параметри спектра  $^{127}\text{I}$  NQR змішаного шаруватого напівпровідника  $\text{Pb}_{1-x}\text{Mn}_x\text{I}_2$ .** *І.Г.Вертегел, Е.Д.Чесноков, О.І.Овчаренко, А.П.Буківський, Ю.П.Гнатенко.*

Приведено результати досліджень концентраційних залежностей параметрів спектра ЯКР  $^{127}\text{I}$  змішаних шаруватих напівпровідників  $\text{Pb}_{1-x}\text{Mn}_x\text{I}_2$ . Показано, що в інтервалі вмісту  $\text{MnI}_2$   $0.00 < x \leq 0.1$  іони  $\text{Mn}^{2+}$  в основному заміщають іони  $\text{Pb}^{2+}$  у кристалічних шарах, а нанокластерна доменна структура  $\text{Pb}_{1-x}\text{Mn}_x\text{I}_2$  приводить до зміни інтегральної інтенсивності спинових ехосигналів ЯКР. Виявлене зменшення часу спин-граткової квадрупольної релаксації ядер  $^{127}\text{I}$  вказує на існування додаткового механізму релаксації. Цей механізм пов'язаний з дипольною взаємодією  $\text{Mn}^{2+}$  з найближчими ядрами  $^{127}\text{I}$ .

## 1. Introduction

Nuclear quadrupole interactions are very sensitive to various crystalline deformations that induce a change of NQR (Nuclear Quadrupole Resonance) frequency. The crystalline

structure of the layered  $\text{PbI}_2$  semiconductors allows the impurities to be located in different crystallographic positions. Previously, it has been shown on the example of  $\text{PbCdI}_2$  crystals that crystalline clusters can form in layered solid solutions [1, 2]. These crys-

talline formations strongly affect on the physical properties of such crystals.

It should be noted that  $\text{PbI}_2$  layered semiconductors relate to the semiinsulating materials. Their physical properties allow one to use these materials for the development of X- and gamma-rays detectors. Earlier the studies of the PL and X-ray diffraction spectra of  $\text{Pb}_{1-x}\text{Mn}_x\text{I}_2$  solid solutions were carried out in [3–6]. Radiospectroscopic investigations of  $\text{Pb}_{1-x}\text{Mn}_x\text{I}_2$  crystals were mainly related with the EPR measurements [7–9] and magneto-optical properties. It was found that the ferromagnetic interaction between the Mn ions takes place both in the interlayer space and in the crystalline layers [9]. At the same time, the antiferromagnetic character of the exchange interaction between Mn ions and holes of the valence band was observed in [10]. The NQR spectra of chemically pure  $\text{PbI}_2$  crystals of 2H- and 4H-polytypes as well as ones intercalated with organic materials have also been investigated in [11–14]. The NQR spectra of  $^{127}\text{I}$  for mixed  $\text{PbI}_2$ -based layered crystals have been investigated in [15–17]. However, the study of the dependence of NQR spectra parameters on Mn concentrations for these crystals was not carried out.

Proceeding from above-stated: the aim of the work was to investigate the mechanism of  $\text{Mn}^{2+}$  ions influence on the structural and physical properties of  $\text{Pb}_{1-x}\text{Mn}_x\text{I}_2$ . For this purpose, the  $^{127}\text{I}$  NQR spectra parameters of the concentration dependence were measured. To determine the mechanism of the  $^{127}\text{I}$  spin interaction with the  $\text{Pb}_{1-x}\text{Mn}_x\text{I}_2$  crystal lattice, the concentration dependence of the quadrupole spin-lattice relaxation time  $T_1$  was also investigated. For the first time, the concentration dependences of the  $^{127}\text{I}$  NQR spectrum ( $\pm 3/2 \leftrightarrow \pm 5/2$ ) parameters of  $\text{Pb}_{1-x}\text{Mn}_x\text{I}_2$  layered semiconductor crystals for different Mn concentrations ( $x = 0.0, 0.03, 0.05, \text{ and } 0.1$ ) were investigated.

## 2. Experimental

The NQR spectra of  $^{127}\text{I}$  for the investigated crystals were measured at 77 K in the frequency range of 5–300 MHz using a pulsed quasi-coherent NQR spin-echo spectrometer. The accuracy of the NQR frequency measurements was determined by the half-widths of the NQR lines and for the investigated crystals this value was not worse than  $\pm 3\text{--}5$  kHz. The measurements of the frequencies  $\nu'$  and  $\nu''$  of  $^{127}\text{I}$  NQR corresponding to transitions  $\pm 1/2 \leftrightarrow \pm 3/2$  and

$\pm 3/2 \leftrightarrow \pm 5/2$  allowed determining the constant  $e^2Qq_{zz}(x)$  of the quadrupole interaction and the parameter  $\eta(x)$  associated with the asymmetry of the gradient electric tensor fields ( $\eta(x) = (q_{xx} - q_{yy})/q_{zz}$ ). The accuracy of determining the asymmetry parameter and the constant quadrupole interaction depends on the width of the line and was not worse than  $\pm 1.5\%$  and  $\pm 0.1\%$ , respectively.

In this work we studied the pure  $\text{PbI}_2$  crystals and  $\text{Pb}_{1-x}\text{Mn}_x\text{I}_2$  solid solutions with the following Mn contents:  $x = 0.03, 0.05, \text{ and } 0.10$ . The investigated crystals were obtained by growing from the melt. It is known [18] that the  $\text{PbI}_2$  crystals obtained by this method are mainly of 2H or 4H polytypes.  $\text{PbI}_2$  crystals of 2H-modification are the most common polytype. This polytype has the spatial group  $D^8_{3a}$  and contains one layer packet (3 atoms) per an elementary cell [20]. The NQR spectrum of  $^{127}\text{I}$  ( $\pm 3/2 \leftrightarrow \pm 5/2$ ) includes only one line with the frequency of  $\nu = 8.930$  MHz at  $T = 77$  K. The 4H polytype of  $\text{PbI}_2$  consists of two layer packets (6 atoms) per an elementary cell and belongs to the spatial  $C^4_{6v}$  group. For such crystals, the NQR spectrum of  $^{127}\text{I}$  in the 4H polytype ( $\pm 3/2 \leftrightarrow \pm 5/2$ ) consists of two lines with NQR frequencies of 9.8 MHz and 10.3 MHz [11]. The presence of two lines in the NQR spectrum indicates two non-equivalent positions of the  $^{127}\text{I}$  nucleus in the elementary cell and fully corresponds to the structure of this polytype. The measurements of  $^{127}\text{I}$  NQR spectra lines integral intensity was fulfilled in the same operating mode of the spectrometer. Obtained integral intensity values were re-counted to type mass unit of  $\text{Pb}_{1-x}\text{Mn}_x\text{I}_2$  materials under investigation.

## 3. Results and discussion

We have found that for  $\text{PbI}_2$  crystals at  $T = 77$  K, the frequencies of  $^{127}\text{I}$  NQR are  $\nu_1$  ( $1/2 \leftrightarrow \pm 3/2$ ) = 4.465 and  $\nu_2$  ( $\pm 2/3 \leftrightarrow \pm 2/2$ ) = 8.935 MHz. These values of the  $^{127}\text{I}$  NQR frequencies correspond to the quadrupole interaction constant  $e^2Qq_{zz} = 29.830$  MHz and the asymmetry parameter of the electric field gradient tensor  $\eta = 0$ . The obtained data are consistent with the results represented in [11] and indicate that the investigated crystals in the range of  $0.00 \leq x \leq 0.05$  have a structure of 2H polytype, which is most stable at room temperature.

As can be seen from Fig. 1, the NQR spectrum of  $^{127}\text{I}$  ( $\pm 3/2 \leftrightarrow \pm 5/2$ ) at  $x = 0, x = 0.03$

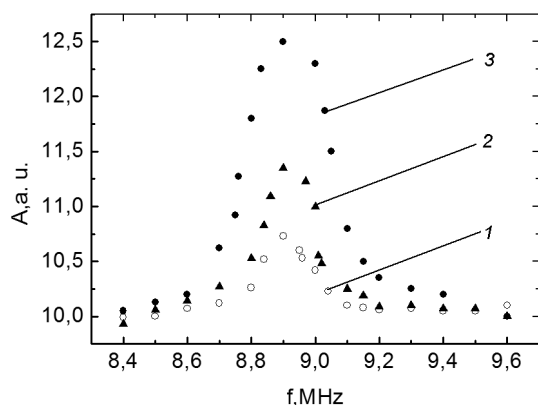


Fig. 1. The NQR spectrum of  $^{127}\text{I}$  for  $\text{PbI}_2$  crystal of 2H polytype (line 1),  $\text{Pb}_{0.97}\text{Mn}_{0.03}\text{I}_2$  (line 2), and  $\text{Pb}_{0.95}\text{Mn}_{0.05}\text{I}_2$  (line 3).

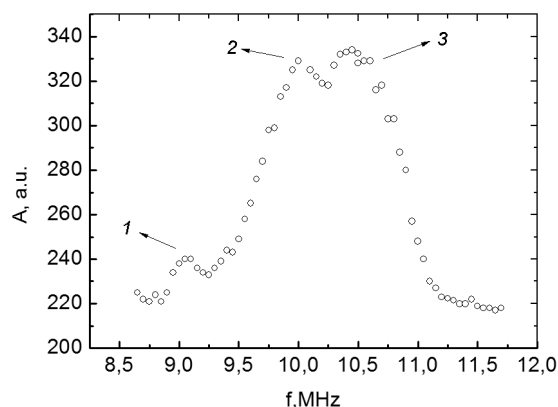


Fig. 2. NQR spectrum of  $^{127}\text{I}$  for  $\text{Pb}_{1-x}\text{Mn}_x\text{I}_2$  crystal with  $x = 0.1$ , 1 —  $^{127}\text{I}$  spectrum line of 2H polytype; 2, 3 — spectrum lines of 4H polytype.

and  $x = 0.05$  for the  $\text{Pb}_{1-x}\text{Mn}_x\text{I}_2$  crystals consists of one line with frequency  $\nu = 8.930 \pm 0.005$  MHz. With an increase in the content of Mn atoms in the  $\text{Pb}_{1-x}\text{Mn}_x\text{I}_2$  crystal, the width of the  $^{127}\text{I}$  NQR line ( $\pm 3/2 \leftrightarrow \pm 5/2$ ) increases significantly. At the same time, with increasing content of Mn to  $x = 0.05$ , the frequency of the  $^{127}\text{I}$  NQR line does not change (see Table), but its width is almost doubled. Since the frequency of the  $^{127}\text{I}$  NQR line ( $\pm 3/2 \leftrightarrow \pm 5/2$ ) for the values  $0 \leq x \leq 0.05$  does not change, this means that the crystallographic positions of Mn atoms remain unchanged. The obtained results show that for  $\text{Pb}_{1-x}\text{Mn}_x\text{I}_2$  crystals with  $0 \leq x \leq 0.05$ ,  $\text{Mn}^{2+}$  ions preferably replace  $\text{Pb}^{2+}$  ions in the crystalline layers; this causes a change in the width of the  $^{127}\text{I}$  NQR line, but does not change the NQR frequency of  $^{127}\text{I}$  line ( $\pm 3/2 \leftrightarrow \pm 5/2$ ).

As the Mn content increased in the  $\text{Pb}_{1-x}\text{Mn}_x\text{I}_2$  crystal up to  $x = 0.1$ , the  $^{127}\text{I}$  NQR spectra considerably differed from the previous spectra at  $x = 0.0, 0.03$ , and  $0.05$ . This difference is connected with the fact, that the crystals with  $x = 0.1$  have the heterogeneous composition consisting of 2H and 4H polytypes, while the crystals with  $0.00 \leq x \leq 0.05$  contain only a 2H modification.

Table

$\text{Pb}_{1-x}\text{Mn}_x\text{I}_2$	The width of NQR line $\Delta\nu$ , MHz	Frequency $\nu$ ( $\pm 3/2 \leftrightarrow \pm 5/2$ ), MHz
$x = 0.0$	0.190	8.935
$x = 0.03$	0.218	8.930
$x = 0.05$	0.468	8.932
$x = 0.1$	0.9	9.025

The NQR spectrum ( $\pm 3/2 \leftrightarrow \pm 5/2$ ) shown in Fig. 2 has three lines at the following frequencies:  $\nu_1(1) = 9.03$  MHz,  $\nu_2(2) = 10.00$  MHz, and  $\nu_3(3) = 10.50$  MHz. According to [11], the NQR spectrum of  $\text{PbI}_2$  for the 4H modification consists of two lines of approximately same intensity with frequencies  $\nu_1 = 9.8$  MHz and  $\nu_2 = 10.3$  MHz. It should be noted that the 4H polytype formation in most cases is caused by the presence of impurity atoms. The obtained NQR spectrum of  $^{127}\text{I}$  for  $\text{Pb}_{1-x}\text{Mn}_x\text{I}_2$  crystals ( $x = 0.1$ ) shows that the investigated crystals have a heterogeneous composition including 4H polytype crystals (lines 2 and 3, Fig. 2) and 2H polytype ones (line 1, Fig. 1). In this case, the frequency of the NQR spectrum of all three lines increases with respect to the frequencies of the NQR spectrum of pure  $\text{PbI}_2$  crystals by the value of about 200 kHz (2 % of absolute values). The shifting of the NQR frequency may be due to the Zeeman effect associated with the ferromagnetic properties of the part of the manganese ions.

It is known [19] that the product of the width and intensity of the NQR line is proportional to the quantity of the resonance nuclei, which forms this line. As it is seen in Fig. 1, the integral intensity  $J$  increases with increasing  $\text{Mn}^{2+}$  concentration. If for  $x = 0$ ,  $J = 1$ , then for  $x = 0.03$ ,  $J = 4.2$ , for  $x = 0.05$ ,  $J = 10$ , and for  $x = 0.1$ ,  $J = 30$  in the arbitrary units. The intensity increase beginning from  $x = 0.03$  shows the possibility of the formation of nano-clusters — domains, which amplify the NQR echo-signals due to ferromagnetic exchange interaction of  $\text{Mn}^{2+}$ . It is known [21] that if in the crystals there are domains and boundaries of domains, then the local magnetic field acting on the

nuclear spins is 10–100 times greater at the boundaries than within the domains. For the nuclei at the domain boundary, the theoretical estimation based on the experimental results gives the value  $10^3 - 10^4$  for the amplification factor of NMR-NQR spin echoes. The study of the change in the amplification factor of spin echo signals due to the existence of a domain structure in some ferromagnetic semiconductors was performed in [22]. Previously, we have shown [2, 16, 17, 23] that a characteristic peculiarity of the layered  $\text{Pb}_{1-x}\text{Cd}_x\text{I}_2$  and  $(\text{BiI}_3)_{(1-x)}(\text{PbI}_2)_x$  semiconductors is the formation of the nano-cluster structures during their growth; this effects on the spectral parameters of  $^{127}\text{I}$  NQR spectra and thus changes the physical properties of these solid solutions. Thus, we can assume that for the  $\text{Pb}_{1-x}\text{Mn}_x\text{I}_2$  crystal with  $x = 0.03, 0.05,$  and  $0.10,$  the  $\text{MnI}_2$  nano-cluster domains are formed; this fact, due to the ferromagnetic exchange interaction between the Mn ions, leads to a change in the integral intensity of the observed spin echo signals (Fig. 1).

In order to determine the mechanism of the interaction of nuclear spins  $^{127}\text{I}$  with the  $\text{Pb}_{1-x}\text{Mn}_x\text{I}_2$  crystal lattice, we studied the concentration dependence of the spin-lattice nuclear quadrupole relaxation time  $T_1$ . The following  $T_1$  values were determined: for  $x = 0,$   $T_1 = 7.2 \pm 1.4$  ms; for  $x = 0.05;$   $T_1 = 6.6 \pm 1.2$  ms, and for  $x = 0.1;$   $T_1 = 6.05 \pm 1.2$  ms. It was also established that the decrease in the magnetization of the system of nuclear spins has a single-exponential type. It is known [1] that in  $\text{PbI}_2$  crystals at  $T = 77$  K, the main mechanism of spin-lattice relaxation is the modulation of the intracrystalline field by flexural vibrations. Our results indicate that in the crystals under study, for  $x = 0.05$  and  $x = 0.1,$  the thermal modulation of the magnetic dipole interaction of  $\text{Mn}^{2+}$  ions with the nearest  $^{127}\text{I}$  nuclei also acts as a spin-lattice relaxation mechanism.

#### 4. Conclusions

The obtained results of studying the parameters of  $^{127}\text{I}$  NQR spectra for the  $\text{Pb}_{1-x}\text{Mn}_x\text{I}_2$  crystals with Mn concentrations up to 5.0 % show that the crystallographic positions of the  $\text{Mn}^{2+}$  ions are unchanged, and they partially replace the Pb ions. In this work, the possibility of using NQR measurements to identify both 2H and 4H modifications of mixed  $\text{Pb}_{1-x}\text{Mn}_x\text{I}_2$  crystals has been demonstrated. On the base of the investigation of the concentration dependence of spin echo-signals integral intensity,

the possibility of formation of a domain nano-cluster structure in the  $\text{MnI}_2$  content range of  $0.03 \leq x \leq 0.1$  has been shown. The spin-lattice relaxation time decrease evidences the appearance of a new relaxation mechanism, which is connected with the change of the  $\text{Mn}^{2+}$  ions magnetic dipole interaction with nearest  $^{127}\text{I}$  nuclei.

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