Influence of Co^{+2} and Mn^{+2} ions on parameters of the NQR spectrum I^{127} of mixed layered semiconductors based on lead iodide.

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INTRODUCTION.

PbI_2 semiconductor crystals are interesting because they are used to create highly sensitive uncooled materials for X-ray and γ-ray detectors. Layered solid solutions based on PbI_2 can exhibit features associated with the formation of nanostructured materials. Crystals doped with magnetic atoms are interesting for the development of new materials - layered diluted magnetic semiconductors. It is well known that the NQR method is very sensitive to the study of various crystal deformations caused by the presence of impurity atoms in the crystal lattice.

Crystals PbI_2, $Pb_{1-x}Mn_xI_2$ and $Pb_{0.9}Co_{0.1}I_2$ were grown by the Bridgman method. Crystals were synthesized by direct alloying of components in sealed quartz ampoules under vacuum. Impurity atoms Mn and Co were introduced by adding them to the melt. The elements were purified by vacuum sublimation and carefully weighed to obtain the desired concentration of impurities. The quality of the crystals and the phases of the alloys were checked using X-ray diffraction experiments. The report presents the results of studies of the parameters of the I^{127} NQR spectrum for $Pb_{x-1}Mn_xI_2$ ($0 \le X \le 0.05$) 2H polytype and $Pb_{0.9}Co_{0.1}I_2$ (4H polytype).

EXPERIMENTAL RESULTS

Figure 1 shows the ^{127}I (± 3/2 ↔ ± 5/2) NQR spectrum of the $Pb_{x-1}Mn_xI_2$ 2H polytype at T = 77K.

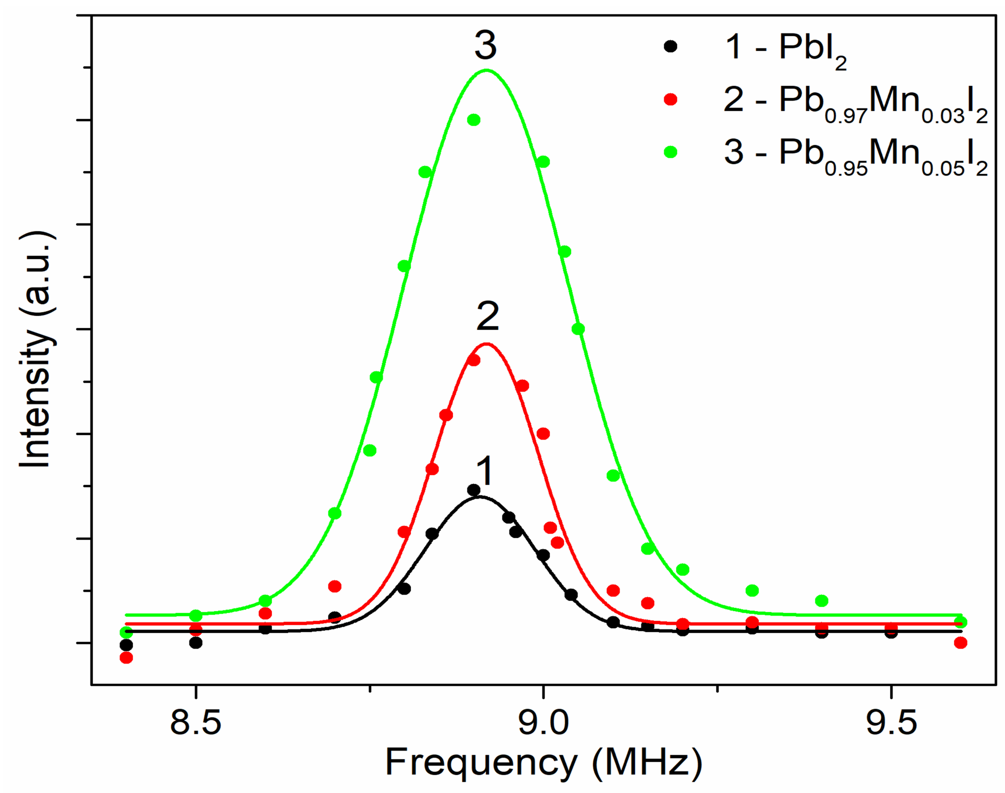

Fig. 1.

As we can see from Fig. 1, the I^{127} NQR spectrum (± 3/2 ↔ ± 5/2) at 77 K for $Pb_{1-x}Mn_xI_2$ 2H crystals consists of one line with a frequency υ = 8.930 ± 0.005 MHz. With an increase in the Mn content in the $Pb_{1-x}Mn_xI_2$ crystal, the width of the I^{127} NQR line (±3/2↔±5/2) significantly increases. At the same time, with an increase in the Mn content from x = 0.00 to x = 0.05, the I^{127} NQR frequency does not change. Since the frequency of the I^{127} NQR line (± 3/2 ↔ ± 5/2) does not change in the range of Mn content 0 ≤x≤ 0.05, this indicates that the crystallographic position of Mn remains unchanged. The results obtained in the range of Mn content 0≤x≤0.05 indicate that in this range of content, Mn2 + ions predominantly replace Pb^{+2} ions in crystalline layers, which leads to a change in the width of the I^{127} NQR line and does not change the value of the I^{127} NQR frequency (± 3/2 ↔ ± 5/2). It is known that the product of the width and the intensity of the NQR line is proportional to the number of resonant nuclei that form a given line. The integral intensity J, as seen in Fig. 1, increases with an increase in the Mn^{+2} concentration. If we assume that for x = 0, J = 1, then for x = 0.03 J = 4.2 and for x = 0.05 J = 10. An increase in intensity starting from x = 0.03 indicates the possibility of formation in crystal of nanocluster-domains, which, due to the ferromagnetic exchange interaction of Mn^{+2}, can amplify the NQR echo signals tens of times.

At the same time, we did not observe changes in the frequency of NQR signals due to the effect on the energy levels of local magnetic fields created by the ferromagnetic properties of Mn^{+2}. For insignificant shifts of the NQR frequency upon doping with manganese, it is probably necessary to take into account not only the ferromagnetic contribution, which leads to an increase in the NQR signal, but also the antiferromagnetic contribution due to the inhomogeneous distribution of Mn over the crystal volume. This contribution decreases the average magnetic field strength over the crystal volume. This can only lead to a slight shift in the NQR frequency of $Pb_{1-x}Mn_xI_2$ as compared to PbJ_2. However, we did not register this shift within the measurement error. At the same time, the signal intensity in compounds with Mn increases. This is evidence of the dominance of the ferromagnetic effect on the system.

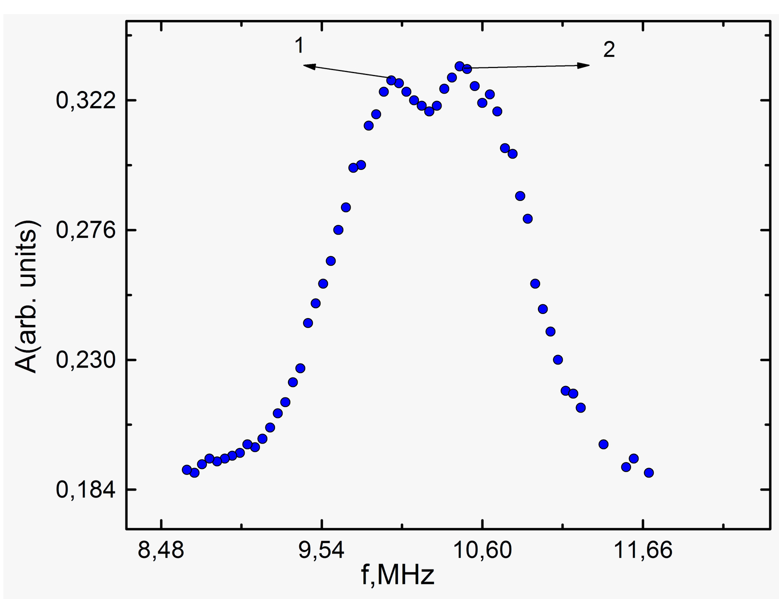

Fig. 2

Crystals of PbI_2 4H polytype include two-layer packets (6 atoms) in a unit cell. For such crystals, the I^{127} PbI_2 NQR spectrum (± 3/2 ↔ ± 5/2) consists of two lines with frequencies of 9.8 and 10.2 MHz. We found that the ^{127}I $Pb_{0.9}Co_{0.1}I_2$ 4H polytype NQR spectrum at 77 K consists of two lines with frequencies of 10.1 and 10.5 MHz (Fig. 2, lines 1 and 2). It can be concluded that there is a slight change in the frequency of the NQR signals. No more than 200 kHz. In this case, the width of the NQR signal is 468 kHz. This indicates that the energy levels of the I^{127} nuclei may undergo insignificant Zeeman splitting in a local magnetic field. This field can be created by the ferromagnetic interaction of cobalt ions. According to [1], CoI_2 crystals have a structure with ferromagnetic balls. It can be assumed that crystalline regions of $Pb_{1-x}Co_xI_2$ with micron surface dimensions and a thickness of several tens of nm are formed in PbI_2. These regions can have ferromagnetic properties and are inhomogeneously distributed in the crystal. According to our estimates, the magnitude of the field created by these nanocrystalline formations cannot exceed $3 \bullet 10^{-3}$ T.

The field can lead to a change in the frequency of the NQR signals by about 200 kHz. We found that for the I^{127} $Pb_{0.9}Co_{0.1}I_2$ NQR spectrum, the total integrated intensity of the lines with x = 0.1 is several times higher than the intensity of the NQR line with x = 0. This result indicates the possibility of the formation of a domain magnetic field in $Pb_{0.9}Co_{0.1}I_2$. If the crystal contains domains and domain walls, then the alternating local magnetic field acting on the nuclear spins in the domain wall is tens of times greater than in the domain. As a result the NQR spin echoes increase so the integrated intensity of the NQR lines increases as well.. Based on this, we can assume that in the $Pb_{1-x}Co_xI_2$ crystal with x = 0.1. $Pb_{0.9}Co_{0.1}I_2$ nanocluster domains are formed, which can have both ferromagnetic and antiferromagnetic nature.

We have investigated the concentration dependence of the spin-spin and spin-lattice relaxation of ^{127}I nuclei to study the influence of Co $^{+2}$ and Mn $^{+2}$ ions on relaxation processes in crystals based on PbI_2. Figure 3 shows the dependences of the fall of the spin echo amplitude A (τ) (on a logarithmic scale) on the interval τ between radio frequency pulses in compounds 1-PbI_2, 2-$Pb_{0.9}Co_{0.1}I_2$, 3-$Pb_{1-x}Mn_xI_2$. This is evidence of the dominance of the ferromagnetic effect on the system.

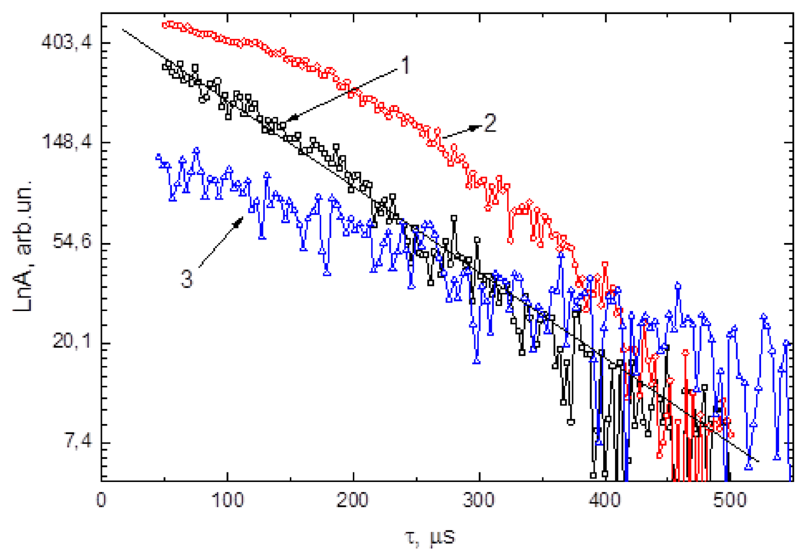

Fig. 3.

As we can see from Fig. 3, the fall rates of LnA (τ) increase with increasing of τ for all three curves. However, for curves 2 and 3 (the time of spin-spin relaxation of ^{127}I nuclei in impurity crystals), the fall of the echo amplitude depends on the delay of the second radio-frequency pulse τ is not exponential. It is known [2] that in compounds with magnetic properties, nonexponential fall of the time T_2 may indicate the contribution of the Sul-Nakamurov interaction. However, low concentrations of Co^{+2} and Mn^{+2} ions in the compounds under study (≤10%) indicate an insignificant probability of such a relaxation mechanism. In [3], we demonstrated that nanocrystalline regions with micron surface dimensions and a thickness of several tens of microns are formed in $Pb_{1-x}Mn_xI_2$. It can be assumed that nanocrystalline regions are also formed in $Pb_{0.9}Co_{0.1}I_2$, which are nonuniformly distributed in the crystal. It is known that microscopically inhomogeneous systems can lead to a different character of the fall A (τ) (the time of transverse spin-spin relaxation T_2). So than, the established nonexponentiality of the time T_2 in $Pb_{x-1}Mn_xI_2$ and $Pb_{0.9}Co_{0.1}I_2$ indicates the inhomogeneity of the distribution of nanocrystalline regions in tested compounds.

Investigation of the influence of Co^{+2} and Mn^{+2} ions on the mechanism of spin-spin relaxation T_2 made it possible to reveal the nonexponential nature of relaxation. The non-exponential nature of the time T_2 indicates the inhomogeneous distribution of nanoclusters in PbI_2.

Conclusions.

1. Studies of the effect of Co^{+2} and Mn^{+2} ions on the I^{127} NQR frequency in PbI2-based compounds indicate that Co^{+2} and Mn^{+2} ions mainly replace Pb^{+2} ions in the crystal layers.
2. The detected increase in the integrated intensity of the I^{127} NQR spectrum lines may indicate the formation of nanocluster magneto-domain structures in the $Pb_{1-x}Mn_xI_2$ and $Pb_{0.9}Co_{0.1}I_2$.
3. The established deviation from the exponential dependence of the spin-spin nuclear relaxation time T_2 indicates the inhomogeneity of the distribution of nanocluster crystal regions in crystals based on PbI_2.

References.

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