

## NQR investigation of crystal structure peculiarities of layered $\text{Pb}_{x-1}\text{Cd}_x\text{I}_2$ semiconductors

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*Received December 2, 2007*

The  $^{127}\text{I}$  NQR spectra of semiconductor mixed crystals  $\text{Pb}_{x-1}\text{Cd}_x\text{I}_2$  at 77 K have been investigated. It is shown that at low values of  $\text{CdI}_2$  concentration, the intra-layer symmetry of the basic crystal becomes distorted considerably. This occurs due to formation of the intra-layer mechanical strains which are defined by the size difference between the main and impurity atoms (Pb and Cd, respectively). At  $x > 0.10$ , intra-layer heterophasic two-dimensional  $\text{CdI}_2$  islets have been shown to be formed. The results are discussed that evidence the formation of amorphous glassy phase of the mixed  $\text{Pb}_{x-1}\text{Cd}_x\text{I}_2$  crystal at  $x > 0.10$ .

Исследованы спектры  $^{127}\text{I}$  ЯКР новых полупроводниковых смешанных кристаллов  $\text{Pb}_{x-1}\text{Cd}_x\text{I}_2$  при 77 К. Показано, что при низких значениях концентрации  $\text{CdI}_2$  происходит существенное искажение внутрислойной симметрии базового кристалла  $\text{PbI}_2$ . Это происходит благодаря формированию внутрислойных механических напряжений, которые определяются различием размеров основных и примесных атомов (соответственно Pb и Cd). Показано, что при  $x > 0,10$  образуются внутрислойные гетерофазные (островковые) структуры  $\text{CdI}_2$ . Обсуждаются результаты, указывающие на образование стеклоподобной аморфной фазы смешанного кристалла  $\text{Pb}_{x-1}\text{Cd}_x\text{I}_2$  при  $x > 0,10$ .

It is known [1–3] that layered semiconductor materials (e.g.,  $\text{CdI}_2$ ,  $\text{PbI}_2$ , having cubic symmetry  $T_d$  [3, 4]), possess some characteristic providing their use as high resolution X-ray detectors at room temperatures. Moreover, those crystals are used successfully in optical and acoustic devices due to their anisotropy of properties. The efficiency of materials used as X-ray detectors is depends on the presence of structure defects and impurities affecting the electronic characteristic and defining radiation resistance of these materials. In this connection, it is of interest to study the mixed crystals  $\text{Pb}_{x-1}\text{Cd}_x\text{I}_2$  and to determine the concentration dependences of parameters defining the changes in the crystal structure and state of the impurities [5, 6]. In

[7], the band structure of the  $\text{PbI}_2$ – $\text{CdI}_2$  system was investigated for the first time at fixed concentrations of components. The results from that work has allowed to extend vastly the possibilities concerning the use of mixed  $\text{PbI}_2$ – $\text{CdI}_2$  crystals, although the concentration dependences of the structure and characteristics have not been studied.

Unlike NQR  $^{127}\text{I}$  spectra of pure  $\text{PbI}_2$  and  $\text{CdI}_2$  crystals [1, 2], the NQR spectra of the mixed crystal are investigated in this work for the first time. The aim of the work is to study the concentration dependences of the  $\text{Pb}_{x-1}\text{Cd}_x\text{I}_2$  mixed crystal structure, which are obtained basing on the analysis of NQR  $^{127}\text{I}$  spectra.

The single  $\text{Pb}_{x-1}\text{Cd}_x\text{I}_2$  crystals were grown by Bridgman method.  $\text{Pb}_{x-1}\text{Cd}_x\text{I}_2$

samples with various contents of  $\text{CdI}_2$  impurity ( $x = 0; 0.02; 0.1; 0.2; 0.4$  and  $0.5$ ) have been investigated. The  $^{127}\text{I}$  NQR spectra of the  $\text{Pb}_{1-x}\text{Cd}_x\text{I}_2$  crystals were obtained using a quasi-coherent pulse radio-spectrometer IS-3 by the double-pulse method in the frequency range 2–30 MHz at 77 K. To detect the weak NQR signals, a digital integrator (storage device) was used. The quadrupole coupling constant  $e^2Qq_{zz}$  and the asymmetry parameter  $\eta$  of the electric field gradient tensor were obtained from tables for two NQR frequencies:  $\nu_1$  and  $\nu_2$ , which correspond to two transitions  $\pm 1/2 \leftrightarrow \pm 3/2$  and  $\pm 3/2 \leftrightarrow \pm 5/2$ , respectively.

It is important to note [1, 2] that, the asymmetry parameter  $\eta$  ( $\eta = (q_{xx} - q_{yy})/q_{zz}$ ) for pure  $\text{PbI}_2$  crystals is zero. This is explained by the fact that the main axes  $q_{xx}$  and  $q_{yy}$  of the electric field gradient tensor lie in planes which coincide with the preferred layers of  $\text{PbI}_2$  crystal. The concentration dependences of the parameter  $\eta$  and quadrupole coupling constants  $e^2Qq_{zz}$  for NQR  $^{127}\text{I}$  bands are presented in the Figure. It follows from the experimental data obtained, when the concentration  $x$  of  $\text{CdI}_2$  impurity in a  $\text{PbI}_2$  crystal increases up to 0.02, the frequencies of the NQR bands for two transitions ( $\nu_1$  and  $\nu_2$ ) at 77 K increase from 4.475 up to 4.700 MHz and from 8.950 up to 9.180 MHz, respectively. This corresponds to the increase of the asymmetry parameter  $\eta$  from zero up to 0.14, while the quadrupole coupling constant  $e^2Qq_{zz}$  increases insignificantly from 29.830 up to 30.708 MHz. In other words, at insignificant amount ( $x \leq 0.02$ ) of the  $\text{CdI}_2$  impurity in a  $\text{PbI}_2$  crystal, the intra-layer symmetry of doped  $\text{Pb}_{1-x}\text{Cd}_x\text{I}_2$  crystals changes essentially, while the inter-layer symmetry changes much less. Thus, the low content of the  $\text{CdI}_2$  impurity in the  $\text{PbI}_2$  crystal matrix can be assumed to result in a significant deterioration of the intra-layer symmetry. At the same time, when  $x \leq 0.02$ , the observed insignificant change of the coupling constant  $e^2Qq_{zz}$ , (relative shift being no more than 0.03) allow to assume that the inter-layer symmetry remains unchanged, so the doped  $\text{Pb}_{1-x}\text{Cd}_x\text{I}_2$  crystals could be presented as layered crystals. The observed intra-layer symmetry deterioration may be connected with size difference between the impurity Cd atoms and isovalent Pb ones forming the basic crystal matrix.

A further increase of the  $\text{CdI}_2$  impurity concentration in the basic matrix of  $\text{PbI}_2$

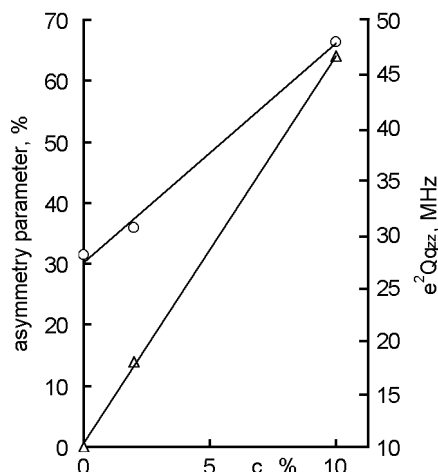


Fig. Concentration dependences of the asymmetry parameter  $\eta$  ( $\eta = (q_{xx} - q_{yy})/q_{zz}$ ) ( $\Delta$ ) and quadrupole coupling constant  $e^2Qq_{zz}$  (O) for  $^{127}\text{I}$  nuclear resonance in  $\text{Pb}_{1-x}\text{Cd}_x\text{I}_2$  crystals.

crystal (up to 0.10) results in a considerable widening of the  $^{127}\text{I}$  NQR bands: the relative broadening of both  $\nu_1$  and  $\nu_2$   $^{127}\text{I}$  NQR bands amounts approximately 0.33. Besides, all the observed  $^{127}\text{I}$  NQR bands have a complex structure including several maxima. The  $^{127}\text{I}$  NQR frequencies for two NQR transitions  $\nu_1$  and  $\nu_2$  are equal to 8.9 and 12.2 MHz, respectively, that correspond to the further increase of NQR spectra parameters at 77 K:  $e^2Qq_{zz} = 43.429$  MHz, and  $\eta = 0.63$ . The obtained experimental data can be explained by formation of doped two-dimensional (heterophasic)  $\text{CdI}_2$  islets inside the layers of the basic matrix  $\text{PbI}_2$  crystal.

At a further increasing of the impurity concentration ( $x > 0.10$ ), the  $^{127}\text{I}$  NQR bands become broader and NQR spectra at 77 K becomes unobservable. The observed disappearing of the  $^{127}\text{I}$  NQR spectra can be explained by formation of a glassy crystal phase. It should be noted that in this case, when  $x < 0.10$ , the relative shift of the quadrupole coupling constant  $e^2Qq_{zz}$  is about 0.30. At the same time, we must note [2, 9], that intercalation of the  $\text{PbI}_2$  crystals with organic molecules results in a significant changing of the quadrupole coupling constant  $e^2Qq_{zz}$  (the corresponding relative shift of the  $e^2Qq_{zz}$  constant being about 10.0). This is possible to be explained under assumption that new inter-layered bonds are formed at intercalation of the  $\text{PbI}_2$  crystal with some organic molecules. As to

$\text{Pb}_{x-1}\text{Cd}_x\text{I}_2$ , no additional (or new) inter-layered bonds are formed at  $x < 0.10$ .

The results obtained by NQR methods for  $\text{Pb}_{x-1}\text{Cd}_x\text{I}_2$  crystals agree with results of our studies of the photoluminescence spectra of those crystals at 4.5 K [8].

Thus, the studies of the NQR  $^{127}\text{I}$  spectra have shown that at low  $\text{CdI}_2$  impurity concentrations ( $x \leq 0.02$ ), the layered symmetry of the base  $\text{PbI}_2$  crystal becomes distorted essentially. This occurs due to formation of the intra-layer mechanical stresses defined by the size difference between the main and doping atoms (Pb and Cd, respectively). It is shown that at  $x < 0.1$ , a further distortion of intra-layer symmetry ( $\eta = 0.63$ ) is due to formation of two-dimensional  $\text{CdI}_2$  (heterophase) islets within the layers of the basic  $\text{PbI}_2$  crystal matrix. It is to note that no additional (or new) inter-layered bonds are formed at the investigated impurity concentrations in  $\text{PbI}_2$  crystal.

Authors wish to thank Dr.A.V.Bondar for his assistance with the measurements.

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## ЯКР дослідження особливостей структури шаруватих напівпровідників $\text{Pb}_{x-1}\text{Cd}_x\text{I}_2$

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Досліджено спектри  $^{127}\text{I}$  ЯКР нових напівпровідникових змішаних кристалів  $\text{Pb}_{x-1}\text{Cd}_x\text{I}_2$  при 77 К. Показано, що при низьких значеннях концентрації  $\text{CdI}_2$  відбувається значне викривлення внутрішньосферної симетрії базового кристала  $\text{PbI}_2$ . Це є наслідком формування внутрішньосферних механічних напруг, котрі визначаються різницею розмірів основних та домішкових атомів (відповідно Pb та Cd). Показано, що при  $x > 0,1$  утворюються внутрішньосферні гетерофазні (острівкові) структури  $\text{CdI}_2$ . Обговорюються питання відносно утворення склоподібної фази змішаного кристала  $\text{Pb}_{x-1}\text{Cd}_x\text{I}_2$  при  $x > 0,1$ .