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The Influence of Crystal Annealing on Orientation Dependence of Nuclear Quadrupole Resonance in InSe

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The dependence of the spectrum intensity on the orientation of crystallographic axes of anisotropic crystal with respect to the magnetic component vector of high-frequency field was studied using NQR method. The existence of residual intensity of the resonance spectrum while $\mathbf{H}_1 \| \mathbf{c}$ indicates the presence of defects in single crystal – blocks with small angular boundaries or other violations of atomic layers. Crystal annealing at the temperature of 550 °C is accompanied by improvement of quality of NQR resonance spectra and diffraction maxima at topograms.

Keywords: NQR, Layered compounds, Crystallographic orientation, Crystal annealing.

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1. INTRODUCTION

Presence of hexagonal symmetry of crystal structure of GaS, GaSe, InSe layered compounds conditions the axial symmetry of the electric field gradient in metal carriers. In this case, degree of asymmetry of the electric field gradient (asymmetry parameter) is $\eta = 0$ [1]. This leads to the situation when maximum intensity of the nuclear quadrupole resonance (NQR) is observed only at orientation of the magnetic field vector of high-frequency spectrometer along atomic layers of the crystal. The given effect can be used for both crystal orientation in the given coordinates and detection of violations and defects of the crystal structure inside the sample.

2. EXPERIMENT AND DISCUSSION

InSe monocrystals grown by the Bridgman method were used to perform the experiment. Observation of the NQR was realized using the pulsed spectrometer with fast Fourier transformation of signals of spin induction of ^{115}In nuclei. Since indium nucleus has spin of $I = 9/2$, then in accordance with the selection rules four resonance transitions exist: $\pm 1/2 \leftrightarrow \pm 3/2$; $\pm 3/2 \leftrightarrow \pm 5/2$; $\pm 5/2 \leftrightarrow \pm 7/2$; $\pm 7/2 \leftrightarrow \pm 9/2$ [1]. Four resonance frequency ranges, whose mean values (10.25; 20.5; 30.8; and 41 MHz) approximately correspond to the ratio of $\nu_1 : \nu_2 : \nu_3 : \nu_4 = 1 : 2 : 3 : 4$, were found in InSe for the isotope ^{115}In.

Ratio of the transition frequencies indicates a slight asymmetry of the electric field gradient on ^{115}In, therefore, its distribution can be considered as the axially-symmetric. Instrumentally convenient frequency range, which corresponds to the transition $\pm 3/2 \leftrightarrow \pm 5/2$, was the most studied in detail. In this case, NQR spectrum of ^{115}In at room temperatures is located in the frequency range of 20.4-20.7 MHz (Fig. 1a, b). In Fig. 1a, b we illustrate the influence of annealing of InSe samples intended for the production of heterophotodiodes based on the *p*-InSe-*n*-InSe structure on the change of NQR spectra. As seen, NQR spectrum in the initial sample (Fig. 1a) is a set of extended resonance lines with fuzzy shape. Annealing of the samples at the temperature of 550 °C during 6 hours significantly changes the form of the NQR spectrum (Fig. 1b). Ordered spectrum, where lines are clearly distinguished that indicates the improvement of the structural perfectness of the samples, is observed in this case.

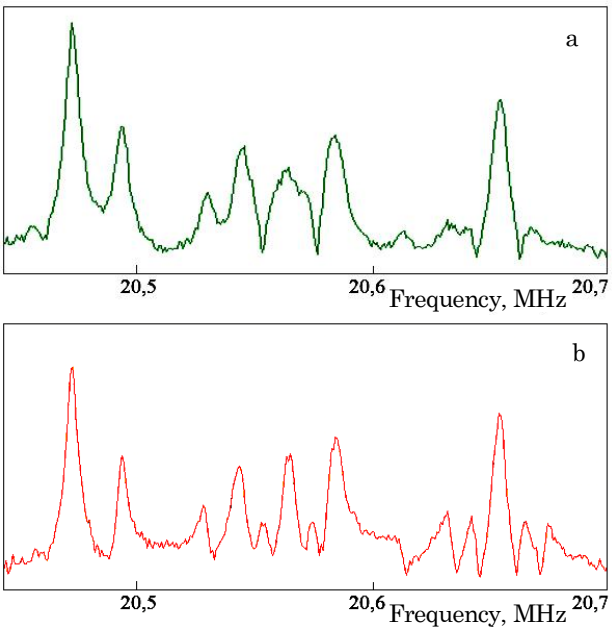

Fig. 1 – NQR spectra of ^{115}In in InSe obtained by fast Fourier transformation of the signals of nuclear spin induction: resonance spectrum in monocrystalline sample before (a) and after (b) annealing

To check the perfectness of monocrystals by method of the orientation dependence, InSe sample was placed in such a way that planes of atomic layers could rotate in high-frequency field of the oscillating circuit coil of spectrometer. We have investigated the dependence of the integral intensity of the resonance spectrum on the angle between the direction of high-frequency field vector $\boldsymbol{H}_1$ and direction of the optical axis $\boldsymbol{c}$ (Fig. 2, inset). In the case of perfect layered crystal structure at $\boldsymbol{H}_1 \| \boldsymbol{c}$ resonance signal is absent, and at $\boldsymbol{H}_1 \perp \boldsymbol{c}$ signal intensity

becomes the maximum one [1, 2]. Presence of defects and crystalline blocks in a real crystal leads to the violation of ordering of atomic layers and is accompanied by the appearance of components of the NQR signal along the ***c*** direction.

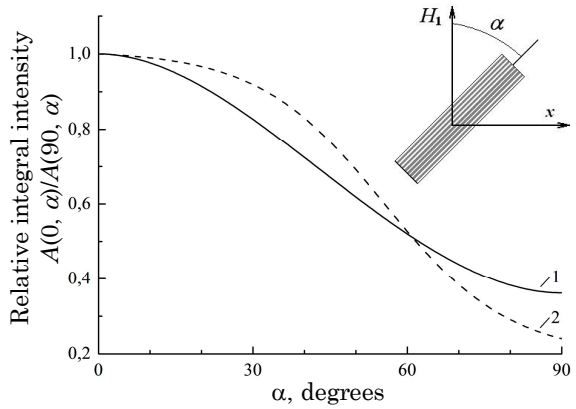

Fig. 2 – Dependence of the integral intensity of the NQR spectrum of ^{115}In on the angle α between atomic plane (0012) and direction of $\boldsymbol{H}_1$ (inset): 1 – InSe monocrystal before annealing; 2 – InSe monocrystal after annealing during 6 hours at the annealing temperature of 550 °C

Investigations have been performed for two samples. For the annealed sample 2 this component is less than for the initial sample 1, therefore, at $\boldsymbol{H}_1 \| \boldsymbol{c}$ curve comes closer to zero values in comparison with the first sample. This implies that at $\boldsymbol{H}_1 \perp \boldsymbol{c}$ signal component is larger in the initial crystal than in the annealed one. Thus, changes in the orientation dependence of NQR along with the transformation in spectra can be used for the investigation of the perfectness of monocrystals.

X-ray topographic investigations of InSe compound have also shown considerable changes in the structural perfectness of crystals during annealing. X-ray topograms taken by the Berg-Barrett method [3] for the initial and annealed crystals are illustrated in Fig. 3. The initial surface is represented by the set of planes {001}, reflection plane – (0012). As seen from the given topograms, structural perfectness is improved during annealing. At the same time, stresses in the crystal do not completely disappear. In this case, separate reflexes which indicate the block structure are observed for the initial sample. We have to note that blocks with insignificant misorientation remain in the annealed sample. Investigations of the orientation dependence of NQR with respect to the magnetic component of high-frequency field shows that during annealing influence of crystalline defects decreases but their action remains appreciable.

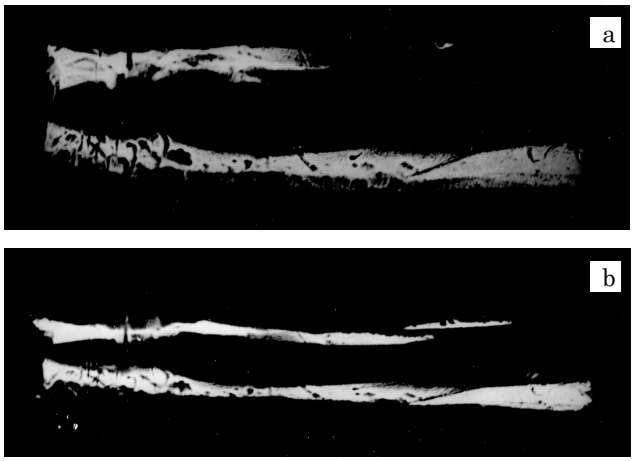

Fig. 3 – X-ray topograms of the InSe sample: a – unannealed sample; b – annealed at $T = 550$ °C during 6 hours. Cu Kα-radiation. Reflection plane (0012)

3. CONCLUSIONS

1. Structure of InSe compound allows to define the gradient axis direction of the crystal electric field from the NQR spectrum intensity and estimate the degree of crystal symmetry based on the ratio of the spin transition frequencies.

2. NQR together with the X-ray diffraction investigations gives the sensitive method for the detection of crystalline blocks with small angular boundaries and other violations in the plane of atomic layers of A^3B^6-type crystals.

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