

# Change of NQR line shape of glassy $\text{As}_2\text{Se}_3$

I. KORNEVA<sup>\*a</sup>, N. SINYAVSKY<sup>a</sup>, M. OSTAFIN<sup>b</sup>, B. NOGAJ<sup>b</sup><sup>a</sup>Baltic State Academy, Molodiozhnaya str. 6, 235029 Kaliningrad, Russia<sup>b</sup>Adam Mickiewicz University, Department of Physics, Umultowska 85, 61-614 Poznan, Poland

The  $^{75}\text{As}$  nuclear quadrupole resonance (NQR) spectra of a powder glassy semiconductor  $\text{As}_2\text{Se}_3$  aged about 20 years were recorded at 77 K. The reconstruction of very broad NQR spectra observed in  $\text{As}_2\text{Se}_3$  by different methods was used. The resultant NQR spectra of  $\text{As}_2\text{Se}_3$  consist of two broad components which were attributed to the two inequivalent sites occupied by  $^{75}\text{As}$  nuclei in a crystalline unit cell and can be explained by a partial crystallization of glassy  $\text{As}_2\text{Se}_3$ .

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## 1. Introduction

Nuclear quadrupole resonance (NQR) has already been successfully applied as a probe of local structure and properties of disordered materials such as amorphous solids and glasses [1,2]. Studies of  $^{75}\text{As}$  NQR line shapes in the chalcogenide glassy semiconductors provide important information about the local bonding of  $^{75}\text{As}$  atoms which facilitates understanding the nature of amorphous state. Taylor *et al.* studied the NQR line shapes in bulk glassy, rapidly evaporated thin films and rapidly drawn  $\text{As}_2\text{Se}_3$  [3-5]. In the present paper various methods of estimation of the NQR line shapes of powder glassy  $\text{As}_2\text{Se}_3$  at 77 K aged for more than 20 years are presented.

## 2. Experimental

The samples of glassy  $\text{As}_2\text{Se}_3$  prepared by the method of quenching from the melt and aged for more than 20 years at room temperature were used for NQR measurements. Glassy samples were then crushed into powder and placed in tubes to fit inside the NQR coil. NQR measurements were made on an FT pulsed NQR spectrometer type NQS-300 made in our laboratory in cooperation with MBC ELECTRONICS (Warsaw, Poland) and using a two-pulse Hahn spin echo sequence ( $\pi/2 - \pi$ ). Duration of the first pulse was 5  $\mu\text{s}$ , an interval between pulses - 80  $\mu\text{s}$ . The Hahn sequence was recycled 1800 times every 100  $\mu\text{s}$ . Consecutive 1800 spin echo signals were digitized at 0.2  $\mu\text{s}$  dwell time and accumulated for the desired signal-to-noise ratio. The  $^{75}\text{As}$ -NQR spectra had to be recorded at 77 K by immersing the samples in liquid nitrogen bath. Otherwise all our attempts to receive any NQR signal at room temperature failed. In order to record the entire NQR spectra, which were wide in excess of 20 MHz, the spectrometer frequency had been incremented by 200 kHz and the corresponding partial NQR signals recorded.

## 3. Results and discussion

All the spin echo signals, recorded for a powder glassy  $\text{As}_2\text{Se}_3$  in the range of frequencies 48.6 MHz - 66.2 MHz are represented in Fig. 1 as 2D spectrum.

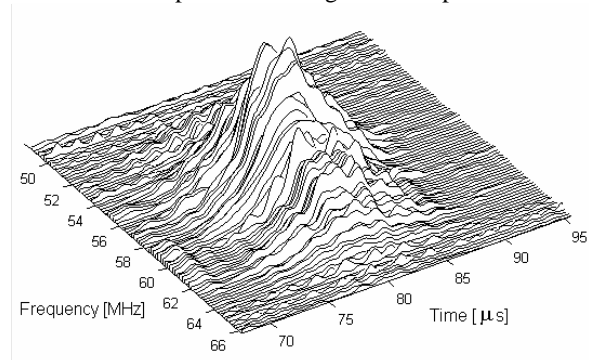


Fig. 1. 2D spectrum of  $^{75}\text{As}$ -NQR spin echo magnitude signals in  $\text{As}_2\text{Se}_3$  plotted in frequency - time coordinates.

The reconstruction of this very wide NQR spectrum has been carried out on the basis of integral intensities of spin-echo signals obtained at each frequency step. To avoid phasing problems a magnitude echo signal  $I_m = \sqrt{u^2 + v^2}$  was calculated using real (u) and imaginary (v) outputs of a phase sensitive quadrature receiver. To reduce a constant component in an NQR spectrum a magnitude signal at each frequency point was calculated as

$$I_m = \sqrt{I_{S+N} - I_N}, \quad (1)$$

where  $I_{S+N}$  is the integral intensity of an echo signal with noise and  $I_N$  is the integral intensity of noise (determined from a tail of an echo signal). Thus the magnitude echo amplitudes given by Eq. 1 and plotted on an appropriate frequency scale constitute a magnitude NQR spectrum. The spectrum obtained that way is shown in Fig. 2. It

shows two characteristic wide lines overlapping each other with maximum amplitudes at 56.5 and 61.5 MHz accordingly which we attribute to a two inequivalent sites of  $^{75}\text{As}$  nuclei in a crystalline unit cell. It is well known that the NQR spectrum of crystalline  $\text{As}_2\text{Se}_3$  [6] consists of two narrow lines and the spectrum of glassy  $\text{As}_2\text{Se}_3$  consists of a single broad line, centered between the two lines in a crystal, one from each of the two inequivalent As sites in the unit cell ( $\nu_Q(1) = 56.07$  MHz (crystalline site 1) and  $\nu_Q(2) = 60.25$  MHz (crystalline site 2)). Comparing a spectrum of glassy  $\text{As}_2\text{Se}_3$  from the paper [6] and our spectrum for a sample, aged more than 20 years, it is possible to draw the following conclusions. As is known, crystal ability of glassy As-Se system is insignificant [7]. However, the greatest ability to crystallization possesses glassy  $\text{As}_2\text{Se}_3$ , as it is observed in our case. Thus, one can say that after more than twenty years there was, perhaps, a partial crystallization of glassy  $\text{As}_2\text{Se}_3$ . The NQR spectrum of the glassy  $\text{As}_2\text{Se}_3$  (Fig. 2) has two peaks corresponding to the two lines in a crystal. In papers [5,6] NQR spectrum was approximated by a Gaussian function, because of small quantity of experimental points available on a curve. Approximation of a spectrum by the sum of exponents (two Gaussian peaks fit):

$$I = I_0 + I_1 \exp\left[-\frac{(\nu - \nu_{01})^2}{2\delta_1^2}\right] + I_2 \exp\left[-\frac{(\nu - \nu_{02})^2}{2\delta_2^2}\right] \quad (2)$$

gives the following parameters:  $I_0 = 0.12 \pm 0.02$ ,  $I_1 = 0.82 \pm 0.02$ ,  $I_2 = 0.29 \pm 0.03$ ,  $\nu_{01} = 56.92 \pm 0.12$  MHz,  $\nu_{02} = 62.29 \pm 0.18$  MHz,  $\delta_1 = 3.00 \pm 0.13$  MHz,  $\delta_2 = 1.48 \pm 0.17$  MHz.

The NQR spectrum obtained by using the amplitudes of echo signals for reconstruction has virtually similar form, where the amplitude of each echo was obtained from its approximation by a Gaussian curve.

For comparison the results of using the spin-echo Fourier-transform mapping spectroscopy (NSEFTMS) method introduced by Bussandri and Zuriaga [8] for broad NQR lines are illustrated by Fig. 3.

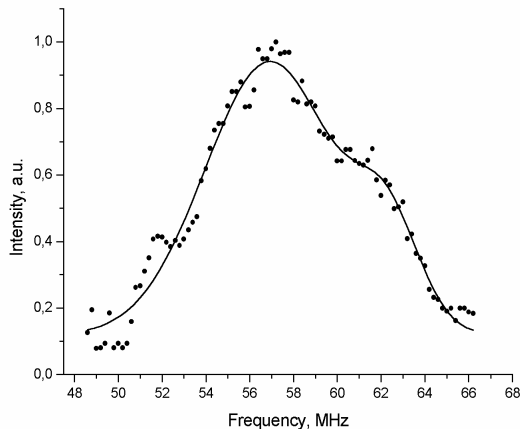


Fig. 2.  $^{75}\text{As}$ -NQR magnitude spectrum of  $\text{As}_2\text{Se}_3$  powder at  $T = 77$  K, obtained by plotting the calculated integral intensities of echo signals shown in Fig. 1.

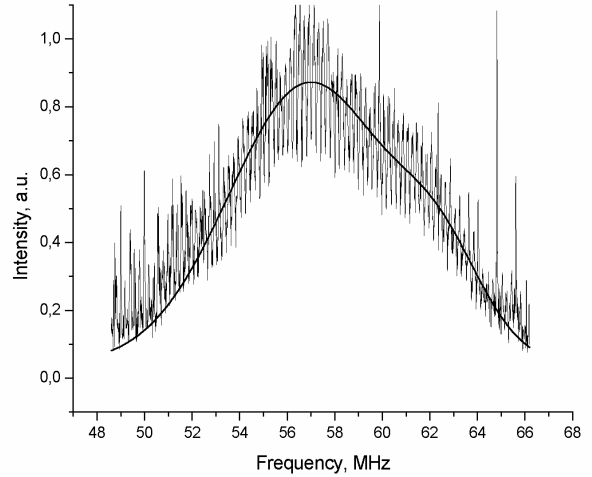


Fig. 3.  $^{75}\text{As}$ -NQR spectrum obtained by a spin-echo mapping spectroscopy method [8]. The solid line shows spectral approximation by two Gaussian peaks with parameters:  $I_0 = 0.18 \pm 0.01$ ,  $I_1 = 0.69 \pm 0.01$ ,  $I_2 = 0.20 \pm 0.01$ ,  $\nu_{01} = 56.93 \pm 0.05$  MHz,  $\nu_{02} = 61.98 \pm 0.07$  MHz,  $\delta_1 = 3.11 \pm 0.06$  MHz,  $\delta_2 = 1.41 \pm 0.08$  MHz.

The NSEFTMS method in NQR consists in accurate reconstruction of virtually deliberately broad NQR spectra by co-adding the partial Fourier-transform spectra taken at  $N$  frequency steps  $\Delta\nu_Q \leq \nu_1$  (called the “mapping” steps), where  $\nu_1 = \gamma\mathcal{H}_1$  is the Larmor frequency of quadrupolar nuclei in a rotating frame and  $N$  mapping steps cover the entire NQR spectrum to be scanned. NSEFTMS provides an efficient alternative to the time-consuming point-by-point scanning technique for the study of broad NQR spectra provided these spectra have some sharp features of higher spectral resolution than the mapping step used. This, however, appeared not to be the case in chalcogenide glassy semiconductors studied here. The frequency step used in our measurements was  $\Delta = 200$  kHz while according to [8] the maximum mapping step should be  $\nu_1 = \gamma\mathcal{H}_1 \approx 60$  kHz in order that distortions were not observable on a spectral line. This would imply reducing the mapping step 3-4 times and thus increasing the duration of experiment to an unacceptable time.

The present results indicate that true  $^{75}\text{As}$ -NQR line shapes can be obtained by using NSEFTMS as well as by simple point-by-point methods using additionally a Gaussian fit estimate of an NQR spin-echo signal. As one can see our results differ from the NQR spectrum of glassy  $\text{As}_2\text{Se}_3$  obtained by P.C. Taylor *et al.* [5,6]. These changes in line shapes are likely to be dependent on age of the sample. Detailed studies of this problem are now in progress.

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\* Corresponding author: kornev@albertina.ru