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AMORPHOUS, VITREOUS, POROUS, ORGANIC, AND MICROCRYSTALLINE SEMICONDUCTORS; SEMICONDUCTOR COMPOSITES

Spectra of Nuclear Quadrupole Resonance in Vitreous Semiconductors

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Abstract—The method of nuclear quadrupole resonance is used to study the chalcogenide semiconductors with compositions As_2Se_3 and $As_{14}Sb_4Se_{27}$. It is shown that partial crystallization occurs in a sample of vitreous As_2Se_3 kept for a long time at room temperature; as a result, a change in the shape of the spectrum of the nuclear quadrupole resonance is observed. The ^{75}As spectrum in vitreous $As_{14}Sb_4Se_{27}$ at a temperature of 77 K is measured for the first time. It is assumed that the ^{121}Sb or ^{123}Sb nuclei can contribute to the broad line of the quadrupole resonance. It is shown that the use of the nuclear spin-echo Fourier-transform mapping spectroscopy for reconstruction of very broad lines of the nuclear quadrupole resonance provides no advantages compared to the method of reconstruction based on the points in the integrated intensity of the echo signals.

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Amorphous semiconductors, in particular, chalcogenide vitreous semiconductors, are widely used in modern technologies of, for example, solar cells, optical memory units, and so on [1, 2]. The use of these materials requires understanding of their physical properties. In this context, the structure of amorphous semiconductors and the nature of processes in these materials are currently the subject of considerable interest. However, in application to these disordered materials, such traditional methods of studies as neutron diffraction, diffraction of X-ray photons, and some other methods are not informative to the sufficient extent. According to the experiments carried out in recent years [3–5], the nuclear quadrupole resonance (NQR) has become an extremely useful tool for studying quite a number of materials based on chacogenides (sulfur, selenium, and tellurium). In contrast to the nuclear magnetic resonance, the NQR frequencies are governed by electrical interactions; therefore, the NQR method makes it possible to study the electric fields at the atoms' nuclei directly rather than implicitly. The extremely high sensitivity of NQR to the smallest variations in the electric field makes it possible to use the NQR for studying a wide range of problems related to the intramolecular and intermolecular interactions. For example, one can use the NQR methods to obtain information about the atomic surroundings, i.e., about the local structure, which is very important for amorphous materials where these is no long-range order. In addition, NQR can also be used to gain information about dynamic processes that occur in vitreous semiconductors. In particular, the detailed information about the structure and properties of these materials can be obtained by analyzing the NQR line shape. The NQR line shape is very sensitive to small variations in the short-range order of the vitreous semiconductor structure. A study using the ^{75}As NQR method [5] for As_2Se_3 glasses in the form of a bulk sample, a thin film, and a fiber made it possible to advance important inferences about variations in the structure of these samples on the basis of the shape of the spectra; in particular, it was concluded that there were no As–As bonds in the fiber-shaped sample.

The objective of this study was to gain insight into the effect of duration of storage of the samples of As_2Se_3 chalcogenide glasses after their preparation on the ^{75}As NQR spectrum and to analyze the ^{75}As NQR spectrum of a vitreous $As_{14}Sb_4Se_{27}$ compound that has not been studied by the NQR method until now; we also intended to investigate whether it is possible to reconstruct the very broad NQR lines in these amorphous materials using radio-frequency spectroscopy.

In this paper, we report the results of using the ^{75}As NQR method to study a sample of vitreous arsenic triselenide (As_2Se_3) stored for a long time after its preparation; we compared these results with the data reported in [4]. In addition, we studied a vitreous $As_{14}Sb_4Se_{27}$ compound for the first time. Prior to the experiment, both samples were kept in an evacuated quartz cell at room temperature for more than 20 years. Before carrying out the NQR measurements, the bulk glass was ground into powder and placed in a standard cell of the NQR spectrometer; the cell was 10 cm in diameter.

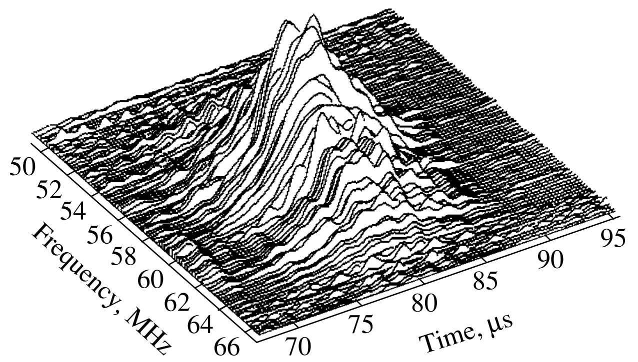

Fig. 1. Three-dimensional image of the echo-signal power after the second pulse on the frequency–time coordinate plane for various frequencies of the ^{75}As NQR spectrum in As_2Se_3.

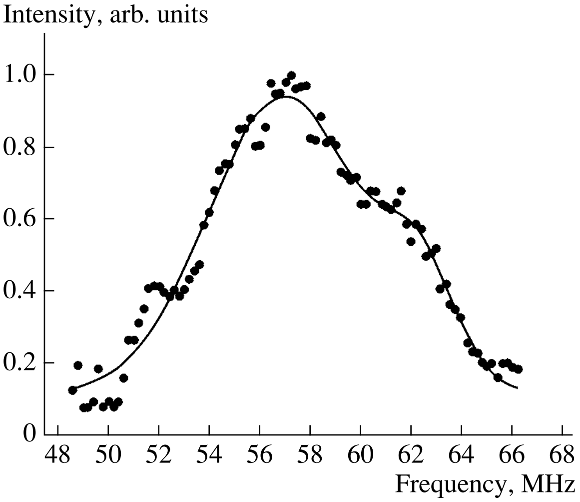

Fig. 2. The ^{75}As NQR spectrum that corresponds to As_2Se_3 at 77 K and is obtained by summing the integrated intensities of the echo signals.

The experiment was carried out using an NQS-300 pulsed NQR Fourier spectrometer produced by MBS ELECTRONICS; the two-pulse train of the Hahn spin-echo signals was employed. For the samples studied, the duration of the first pulse was 4–5 μs, the interval between pulses was 70–80 μs, and the repetition period was 100 ms. The signal-discretization period was 0.2 μs and the number of integrations used was equal to 2000. The measurements were carried out at the liquid-nitrogen temperature (77 K) with simultaneous frequency retuning of the spectrometer with a step of 200 kHz. The very broad ^{75}As NQR spectrum is a characteristic feature of the studied vitreous semiconductors.

A series of spin-echo signals obtained for the vitreous As_2Se_3 compound in the frequency range of 48–66 MHz is shown in Fig. 1 as a three-dimensional image. We reconstructed the very broad spectrum using the points from the integrated intensity of the spin-echo signals. In order to reduce the dc component in the spectrum, we calculated the signal intensity at each point as $I = \sqrt{I_{S+N} - I_N}$, where I_{S+N} is the integrated signal power with noise included and I_N is the integrated noise power (determined from the tail of the echo signal). In this procedure, we used both the real and imaginary components of the signal. The spectrum obtained in this way is shown in Fig. 2. Approximation of the spectrum using the sum of Gaussian functions

$$I = I_0 + I_1 \exp\left[-\frac{(\nu - \nu_{01})^2}{2\delta_1^2}\right] + I_2 \exp\left[-\frac{(\nu - \nu_{02})^2}{2\delta_2^2}\right] \quad (1)$$

yields 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, and $\delta_2 = 1.48 \pm 0.17$ MHz.

A spectrum with almost the same shape was obtained if we used the echo-signal amplitudes for reconstruction. The amplitude of each echo signal was determined from approximation of this signal by a Gaussian curve.

An analysis of the NQR spectrum for the vitreous arsenic triselenide (see Figs. 1, 2) showed the following. The main structural unit of crystalline As_2Se_3 is represented by an almost regular $AsSe_3$ pyramid, with the arsenic atom at the top and three selenium atoms at the base. If the structural units are combined to form the crystal, there are two nonequivalent sites for arsenic and three such sites for selenium. Such pyramidal units are retained in the vitreous state as well. The ^{75}As NQR spectrum of crystalline arsenic triselenide is represented by two narrow lines with frequencies $\nu_1 = 56.07$ MHz and $\nu_2 = 60.25$ MHz that correspond to the first and second nonequivalent sites for arsenic atoms [4]. A comparison of the NQR spectra for the sample stored for a long time and the as-prepared sample [4] showed that these spectra have different shapes. The spectrum of an as-prepared sample of arsenic triselenide is represented by a symmetric curve with the center located between the NQR lines that correspond to a crystalline sample (with frequencies ν_1 and ν_2). Previously [4, 5], the spectrum was represented by a Gaussian curve.

Two broad lines related to two sites occupied by the arsenic nucleus is observed in the NQR spectrum of the chalcogenide glass formed 20 years ago (see Fig. 2); one peak in this spectrum corresponds to the frequency at which the first resonance line of crystalline As_2Se_3 is observed, while the other corresponds to the second resonance line of the same crystal. Thus, we may assume that a modification of the structure of vitreous arsenic triselenide occurred with time; this modification is possibly related to partial crystallization of the sample. As is known, the ability to crystallize is low for glasses of the As–Se system [6]. However, the highest capacity for crystallization among all compounds of the above system is shown by vitreous arsenic triselenide, which is just what is observed in the case under consideration. Thus, it is possible to estimate the degree of crystallization by analyzing the shape of the line in the ^{75}As NQR spectrum.

In Fig. 3, we show the measured ^{75}As NQR spectrum of the vitreous $As_{14}Sb_4Se_{27}$ compound. The curve obtained from integrated spin-echo intensities for various frequencies of the spectrometer is approximated by the Gaussian peak

$$I = I_0 + \frac{I_1}{\delta\sqrt{\pi/2}}\exp\left[-2\frac{(\nu-\nu_1)^2}{\delta^2}\right], \qquad (2)$$

where $I_0 = 0.14 \pm 0.07$, $I_1 = 9.8 \pm 1.9$, $\nu_1 = 55.6 \pm 0.2$ MHz, and $\delta = 11.0 \pm 1.3$ MHz.

The result of reconstruction of the ^{75}As NQR spectrum using the nuclear spin-echo Fourier-transform mapping spectroscopy (NSEFTMS) [7] is also shown in Fig. 3. It was found that the use of the NSEFTMS method for reconstruction of very broad NQR lines does not offer any advantages compared to the method of reconstruction based on the points from the integrated intensity of the echo signals.

It is worth noting that the echo-signal intensity in the case of $As_{14}Sb_4Se_{27}$ is lower than that for the As_2Se_3 sample and the line is broader in the region of low frequencies. It cannot be excluded that a contribution to the line is made by the resonance of ^{121}Sb nuclei (the transition 1/2 → 3/2) or ^{123}Sb nuclei (the transition 1/2 → 3/2). As was mentioned previously [8], it is these transitions that produce the most intense NQR lines for the antimony-containing compounds.

Thus, we showed that two relatively broad lines are observed in the ^{75}As NQR spectrum of a vitreous As_2Se_3 semiconductor stored for a long time; these lines correspond to the resonance lines of crystalline arsenic triselenide, in contrast to the sample of as-prepared sample that features only a single broad line. This observation indicates that the sample has undergone partial crystallization; the degree of crystallization can be determined by analyzing the shape of the spectral lines. We measured for the first time the ^{75}As NQR spectrum for the vitreous $As_{14}Sb_4Se_{27}$ semiconductor at a temperature of 77 K. We assumed that the resonance of the ^{121}Sb or ^{123}Sb nuclei can contribute to the broad resonance line. We showed that the use of the nuclear spin-echo Fourier-transform mapping spectroscopy for reconstruction of very broad NQR lines offers no advantages compared to the method of reconstruction based on the integrated intensity of the echo signals.

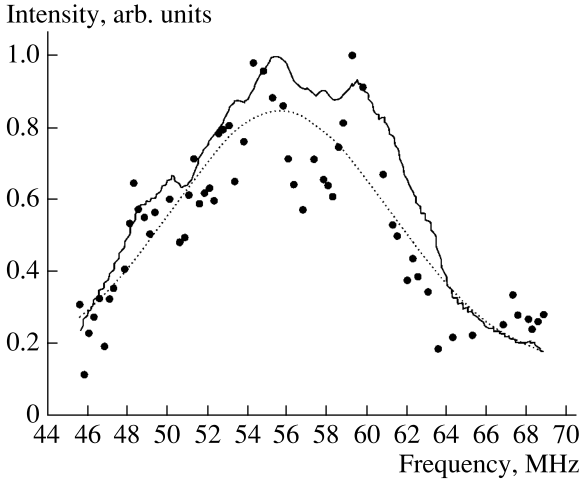

Fig. 3. The ^{75}As NQR spectrum for $As_{14}Sb_4Se_{27}$ at 77 K. The points represent the reconstruction based on the integrated intensity of the echo signals, the dotted line represents the intensity approximation by a Gaussian peak (2), and the solid line represents the results obtained using the NSEFTMS method [7].

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