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Symmetry of the local environment of germanium atoms in amorphous $Ge_2Sb_2Te_5$ films

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The tetrahedral symmetry of the local environment of germanium atoms in amorphous $Ge_2Sb_2Te_5$ films has been demonstrated by the method of Mossbauer spectroscopy on the ^{73}Ge isotope.

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Materials with phase transition based on chalcogenide alloys $Ge_2Sb_2Te_5$ (GST) are widely used for storage and coding of data. To develop new materials, corresponding to the requirements of high density and miniaturization of the memory devices, it is necessary to understand the details of their microstructure and related distortions both in crystalline and amorphous states.

Kolobov et al. [1] based on the research of the extended X-ray absorption fine structure (EXAFS) by the spectroscopy method believed that amorphization of the GST alloy under the action of the laser emission was accompanied by a jump of the germanium atom from the octahedral positions occupied in the crystal, into tetrahedral positions, besides, in both phases the Ge and Sb atoms are only related to Te atoms. Baker et al. [2], researching in the same manner the amorphous GST, produced by sputtering, found a considerable share of bonds Ge−Ge in addition to the regular bonds Ge−Te. Caravati and Bernasconi [3], proceeding from the modeling results from the first principles of the amorphous GST, produced by tempering from a fluid phase, found that in its structure one third of Ge atoms is in tetrahedral environment, while the remaining Ge, Sb and Te atoms have defective octahedral environment, which reminds the environment of these atoms in the crystalline GST. Liu et al. [4] using high-resolution transmission electron microscopy and X-ray diffraction demonstrated the coexistence of octahedral and tetrahedral coordinated germanium cations in the structure of the crystalline GST, besides, the share of the tetrahedral Ge of the total Ge quantity for different specimens was from 0.32 to 0.37. Authors [5], using the principles of molecular dynamics within the density functional theory, found that in the structure of vitriform GST the Ge atoms are in a tetrahedral net, even though a large part of the Ge atoms is also found in defective octahedrons, besides, tetrahedrons were clearly prevalent. Finally, in the paper by Hosokawa et al. [6] on the abnormal scattering of X-rays it was found that approximately half of the Ge atoms had octahedral environment in the amorphous phase of GST, with this environment being similar to the one in the crystal, and the remaining part of the Ge atoms with the tetrahedral symmetry acted as an energy barrier between the phases, providing for long-term lifetime of the amorphous GST phase.

The available conflicts in the interpretation of the experimental results specify the need to use the experimental methods that are more sensitive to minor changes in the electronic structure of the atoms during the phase transition from the amorphous to the crystalline state. The effective tool to detect the changes in the local environment of atoms and their electron structure in amorphization of $Ge_2Sb_2Te_5$ compound was Mossbauer spectroscopy (MC) on ^{125}Te, ^{121}Sb and ^{119}Sn isotopes [7]. In particular, Mossbauer research on an impurity probe ^{119}Sn made it possible to conclude on the change in the symmetry of the local environment of germanium atoms in the process of crystal–amorphous state transition in the $Ge_2Sb_2Te_5$ alloy. However, this conclusion was based on the assumptions of the isovalent substitution of germanium atoms with stanum atoms in the crystalline and amorphous films.

That is why it seemed feasible to study the local structure of the near environment of germanium atoms in amorphous films of $Ge_2Sb_2Te_5$ alloy, using MC on ^{73}Ge atoms. However, it should be noted that despite the essentially large capabilities of MC on ^{73}Ge isotope for the studies of such kind, the total number of publications on this isotope is small due to the problems related to the difficulties in the registration of various valent states of germanium in one experimental spectrum.

Pfeiffer and Kovacs completed the first calibration of the isomer shift of ^{73}Ge spectra, using Ge:^{73}As source and single-crystal absorber ^{73}Ge [8]. Later Pfeiffer et al. [9]

observed the Mossbauer effect for ^{73}Ge nuclei introduced into the assemblies of Si and Ge single crystal lattices in the process of laser radiation, and concluded that isomer shift of Si:^{73}As spectrum relative to Ge:^{73}As spectrum was so great, that it doubted their own calibration of ^{73}Ge isomer shift done in [8]. Therefore, Svane [10] calculated electron densities on Ge nuclei in assemblies of Ge and Si crystals and, using experimental isomer shifts from [9], received for the isomer shift 13.3 keV in ^{73}Ge the calibration coefficient $\alpha = 0.74\,\text{mm}\cdot\text{s}^{-1}\cdot a_0^3$, where a_0 — Bohr radius. This result makes it possible to hope for the record sensitivity of the ^{73}Ge spectral line position to small changes in the electron structure.

However, when the α coefficient was calculated in [10], the value of Si:^{73}As isomer shift relative to Ge:^{73}As was accepted as equal to IS $= -685\,\mu$m/s, however, paper [9] provides values of the opposite sign. This created an additional motif for our study of the local structure in the near environment of germanium atoms in the amorphous films of $Ge_2Sb_2Te_5$ alloy, and we will use both IS signs in the discussion of our results.

$Ge_2Sb_2Te_5$ compound was synthesized from elemental substances in quartz tubes vacuumized to 10^{-3} mm Hg at 1050 °C. The synthesis involved ^{73}Ge isotope with enrichment of $\sim 70\,\%$. X-ray amorphous films $Ge_2Sb_2Te_5$ with thickness of 20 μm were produced by the method of magnetron sputtering of synthesized polycrystalline specimens on DC in the nitrogen atmosphere on the aluminum foil substrates. Then the films were annealed in the temperature range of 150–200 °C to produce polycrystalline specimens. The film composition was monitored by X-ray fluorescence analysis.

The radioactive isotope ^{73}As for the preparation of the Mossbauer source was obtained using ^{74}Ge$(p, 2n)^{73}$As reaction. Mossbauer sources Ge:^{73}As were prepared on the basis of the single-crystal Ge film (^{73}As diffusion in the hydrogen flow at 800 °C for 20 h). Mossbauer spectra were measured on CM 4201 TerLab spectrometer at 295 K.

Mossbauer spectra of amorphous and polycrystalline $Ge_2Sb_2Te_5$ films are presented in fig. 1. You can see that in the experiment it was possible to record only the spectrum of the amorphous absorber with $-95(15)\,\mu$m/s isomer shift relative to the Ge:^{73}As source in the selected range of Doppler speeds.

Therefore, the expected advantage of the high MC sensitivity on ^{73}Ge isotope to the changes in the electron structures turned into experimental complications. However, the fact that with the Ge:^{73}As source only the spectrum of amorphous absorber is recorded, indicates the closeness of electron structures of ^{73}Ge atoms in the single-crystal germanium (atoms have the tetrahedral system of chemical bonds) and in the amorphous $Ge_2Sb_2Te_5$ alloy. This is confirmed by the conclusion made on the basis of MC data on impurity atoms ^{119}Sn regarding the stabilization of germanium atoms in the amorphous $Ge_2Sb_2Te_5$ alloy in the tetrahedral coordination [7]. It also indirectly confirms the conclusion [7] on the substantial difference of the near

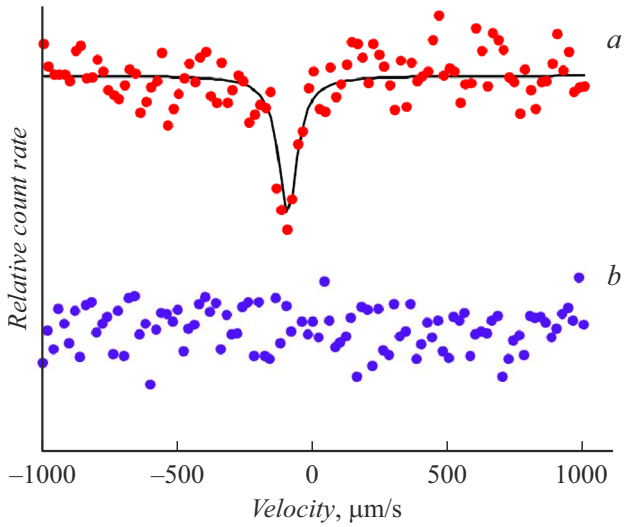


Figure 1. Mossbauer spectra ^{73}Ge of amorphous (*a*) and polycrystalline (*b*) $Ge_2Sb_2Te_5$ films at 295 K with Ge:^{73}As source.

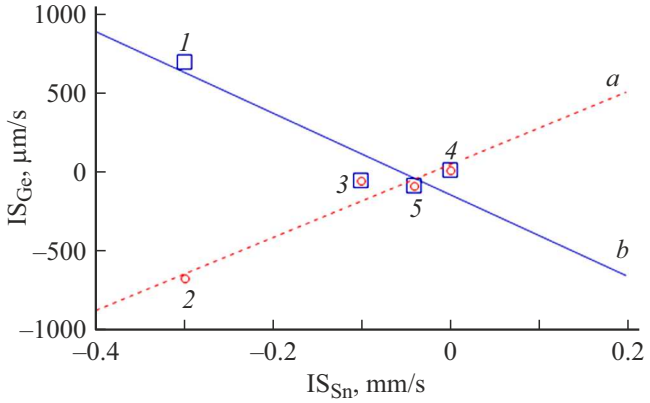


Figure 2. Ratios between isomer shifts of Mossbauer spectra of ^{119}Sn (IS$_{Sn}$) and ^{73}Ge (IS$_{Ge}$) atoms in single crystal silicon (*1, 2*), copper (*3*), germanium (*5*) and in amorphous $Ge_2Sb_2Te_5$ film (*4*) for IS$_{Ge}$ in Si, equal to $-685\,\mu$m/s (straight line *a*) and $+685\,\mu$m/s (straight line *b*). Experimental data for ^{73}Ge were taken from [8,9] and for ^{119}Sn — from [11].

environment and, accordingly, electron structures of Ge atoms in crystalline and amorphous $Ge_2Sb_2Te_5$ films.

To assess the possible position of ^{73}Ge spectrum in the crystalline film and for joint interpretation of MC results on ^{73}Ge and ^{119}Sn isotopes, an attempt was made to find the correlation ratios between the isomer shifts of both Mossbauer isotopes. The prerequisite for their search would be the estimates of electron densities in the nuclei of Ge and Sn impurities in the same matrices, which show the linear correlation between these values [10].

In fig. 2 these data are applied on the curve in the coordinates of ^{73}Ge isomer shift (relative to crystalline Ge) IS$_{Ge}$–isomer shift ^{119}Sn (relative to α-Sn) IS$_{Sn}$ in silicon, germanium and copper matrices. Experimental data for ^{73}Ge were taken from [8,9] and for ^{119}Sn — from [11].

Besides, the values of ^{73}Ge isomer shift in Si were placed on the curve with both signs (as discussed above). They may be approximated by two linear functions

$$IS_{Ge}\,[\mu m/s] = 2309\,IS_{Sn}\,[mm/s] + 43.3, \qquad (1)$$

$$IS_{Ge}\,[\mu m/s] = -2583\,IS_{Sn}\,[mm/s] - 152.4. \qquad (2)$$

Straight line a complies with ratio (2) and ^{73}Ge isomer shift in Si $IS_{Ge} = -685\,\mu$m/s, and straight line b — with ratio (1) and ^{73}Ge isomer shift in Si $IS_{Ge} = +685\,\mu$m/s.

Both ratios — (1) and (2) — when the isomer shift of Mossbauer spectrum ^{119}Sn for the polycrystalline film $IS_{Sn} = 1.5$ mm/s is substituted in them [7] provide the same absolute value of ^{73}Ge Mossbauer spectrum isomer shift for this film: $IS_{Ge} \sim 3.6$ mm/s. And (1) causes its positive sign, while (2) — the negative one.

Therefore, the selection of one of ratios (1) or (2) is not of essential value for the assessment of the range of suggested ^{73}Ge spectrum positions in the crystalline film $Ge_2Sb_2Te_5$. However, it may be important in determination of ^{73}Ge nuclear characteristics. Svane [10] accepted ^{73}Ge isomer shift in Si to be equal to $-685\,\mu$m/s, which corresponds to the ratio (2), and received the relative change of the charge radius for the transition to level of 13.3 keV $\Delta R/R = 1.7 \cdot 10^{-3}$. If the isomer shift value $+685\,\mu$m/s specified in [9] is used, it results in the ratio (1). Negative inclination of straight line b in fig. 2 definitely indicates the opposite signs $\Delta R/R$ for ^{119}Sn and ^{73}Ge. In this case the value $\Delta R/R$ for ^{73}Ge must be accepted as equal to $-1.9 \cdot 10^{-3}$.

Conflict of interest

The authors declare that they have no conflict of interest.

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