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Analysis of the local structure of the nearest environment of germanium atoms in chalcogenide alloys $Ge_2Sb_2Te_5$ using the Mössbauer spectroscopy method

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Abstract. The tetrahedral symmetry of the local environment of germanium atoms in amorphous $Ge_2Sb_2Te_5$ films has been demonstrated by Mössbauer spectroscopy in a ^{73}Ge isotope. We conclude that there is a significant difference in the immediate environment and, consequently, in the electronic structures of Ge atoms in crystalline and amorphous $Ge_2Sb_2Te_5$ films. X-ray amorphous $Ge_2Sb_2Te_5$ films with a thickness of 20 μm were obtained by magnetron sputtering of synthesized polycrystalline samples at direct current in a nitrogen atmosphere onto aluminum foil substrates. The films were then annealed in the temperature range of 150–200 °C to obtain polycrystalline samples. The composition of the films was controlled by X-ray fluorescence analysis.

Keywords: Mössbauer spectroscopy, $Ge_2Sb_2Te_5$, local environment of Ge, magnetron sputtering, X-ray fluorescence analysis

Introduction

Phase transition materials based on $Ge_2Sb_2Te_5$ chalcogenide alloys (GST) are widely used for data storage and encoding. To develop new materials that meet the requirements of high density and miniaturization of storage devices, one should understand the details of their microstructure and related distortions in both crystalline and amorphous states. Based on the *X*-ray absorption fine structure spectroscopy (*EXAFS*) study, it was believed that the amorphization of the GST alloy under laser radiation is accompanied by a jump of the germanium atom from octahedral positions occupied in the crystal to tetrahedral positions, and in both phases the Ge and Sb atoms are bound only to Te atoms (Kolobov et al. 2004). Using the same method, amorphous GST obtained by sputtering revealed a significant proportion of Ge–Ge bonds in addition to the usual Ge–Te bonds (Baker et al. 2006). Based on the results of modeling from the first principles of amorphous GST obtained by quenching from the liquid phase, Caravati S. and Bernasconi M. found out that one third of the Ge atoms in its structure are in a tetrahedral

environment, while the remaining Ge, Sb, and Te atoms have a defective octahedral environment, reminiscent of the environment of these atoms in crystalline GST (Caravati, Bernasconi 2007). Liu X. et al. demonstrated the coexistence of octahedral and tetrahedral coordinated germanium cations in the structure of crystalline GST using high-resolution transmission electron microscopy and X-ray diffraction, with the proportion of tetrahedral Ge to the total amount of Ge ranging from 0.32 to 0.37 for different samples (Liu et al. 2011). Using the principles of molecular dynamics within the framework of density functional theory, A. Bouzid et al. established that in the structure of glassy GST, Ge atoms are located in a tetrahedral grid, although a considerable proportion of Ge atoms are also found in defective octahedra, with tetrahedra clearly predominating (Bouzid et al. 2017). Finally, in J. Stellhorn et al., anomalous X-ray scattering revealed that approximately half of the Ge atoms in the amorphous GST phase have an octahedral environment similar to that in a crystal, while the remaining part of the Ge atoms with tetrahedral symmetry acts as an energy barrier between the phases, ensuring a long lifetime of amorphous GST (Stellhorn et al. 2020).

The existing contradictions in the interpretation of the experimental results indicate the need to use experimental methods that are more sensitive to minor changes in the electronic structure of atoms during the phase transition from an amorphous to a crystalline state. Mössbauer spectroscopy (MS) on isotopes ^{125}Te, ^{121}Sb, and ^{119}Sn proved to be an effective tool for detecting changes in the local environment of atoms and their electronic structure during amorphization of the $Ge_2Sb_2Te_5$ compound (Marchenko et al. 2023). In particular, the Mössbauer study on the ^{119}Sn impurity probe led us to a conclusion that the symmetry of the local environment of germanium atoms changed during the crystal-amorphous transition in the $Ge_2Sb_2Te_5$ alloy. However, this conclusion was based on assumptions about the isovalent substitution of germanium atoms with tin atoms in crystalline and amorphous films.

That is why it seemed advisable to study the local structure of the germanium atom layer in amorphous $Ge_2Sb_2Te_5$ alloy films using MS on ^{73}Ge atoms. However, it should be noted that despite the fundamentally great possibilities of MS based on the ^{73}Ge isotope for studies of this kind, publications on this isotope are scarce due to the problems associated with the difficulties of registering various valence states of germanium in one experimental spectrum.

Pfeiffer and Kovacs performed the first calibration of the isomeric shift of the ^{73}Ge spectra using a Ge:^{73}As source and a ^{73}Ge monocrystalline absorber (Pfeiffer, Kovacs 1981). Later, Pfeiffer et al. observed the Mössbauer effect for ^{73}Ge nuclei introduced into the lattice sites of Si and Ge single crystals during laser irradiation (Pfeiffer et al. 1983), concluding that the isomeric shift of the Si:^{73}As spectrum relative to the Ge:^{73}As spectrum is so large that it casts doubt on their own calibration of the ^{73}Ge isomeric shift performed in (Pfeiffer, Kovacs 1981). In this regard, A. Svane calculated the electron densities on Ge nuclei in the nodes of Ge and Si crystals (Svane 1988) and, using experimental isomeric shifts from (Pfeiffer et al. 1983), obtained the calibration coefficient $\alpha = 0.74$ mm s^{-1} a_0^3 for the isomeric transition of 13.3 keV to ^{73}Ge, where a_0 is the Bohr radius. This result gives hope of a record sensitivity of the position of the ^{73}Ge spectral line to small changes in the electronic structure.

However, when calculating the α coefficient in (Svane 1988), the value of the Si:^{73}As isomeric shift relative to Ge:^{73}As was assumed to be IS = –685 μm/s, although in (Pfeiffer et al. 1983) the value of the opposite sign is given. This created an additional motive for our investigation of the local structure of the near germanium atoms in amorphous $Ge_2Sb_2Te_5$ alloy films. When discussing our results, we will use both IS signs.

Experimental technique

The compound $Ge_2Sb_2Te_5$ was synthesized from elementary substances in quartz ampoules evacuated to 10^{-3} mmHg at 1050 °C. The synthesis used the isotope ^{73}Ge with an e enrichment of 70%. X-ray amorphous $Ge_2Sb_2Te_5$ films with a thickness of 20 μm were obtained by magnetron sputtering of synthesized polycrystalline samples at direct current in a nitrogen atmosphere onto aluminum foil substrates. The films were then annealed in the temperature range of 150–200 °C to obtain polycrystalline samples. The composition of the films was controlled by *X*-ray fluorescence analysis.

The radioactive isotope ^{73}As for the preparation of the Mössbauer source was obtained by the reaction ^{74}Ge(p, 2*n*)^{73}As. The Mössbauer sources Ge:^{73}As were prepared on the basis of a Ge monocrystalline film (^{73}As diffusion in a hydrogen stream at 800 °C for 20 hours). The Mössbauer spectra were measured with a CM 4201 TerLab spectrometer.

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Experimental results and their discussion

The Mössbauer spectra of amorphous and polycrystalline $Ge_2Sb_2Te_5$ films are shown in Fig. 1. We can see that the experiment made it possible to register only the spectrum of an amorphous absorber with an isomeric shift of –95(15) μm/s relative to the Ge:^{73}As source in the selected Doppler velocity range.

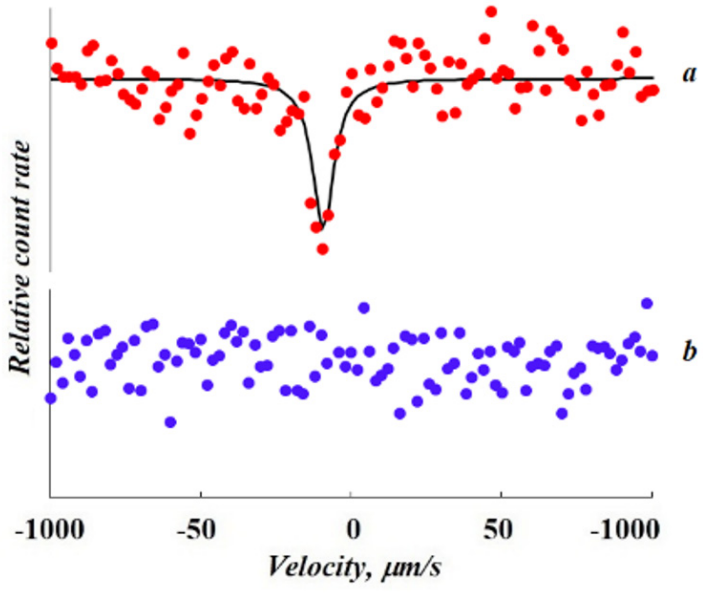

Fig. 1. Mössbauer ^{73}Ge spectra of amorphous (a) and polycrystalline (b) $Ge_2Sb_2Te_5$ films at 295 K with a Ge:^{73}As source

Thus, the expected advantage of the high sensitivity of MS on the Ge^{73} isotope to changes in the electronic structure translated into experimental difficulties. However, the fact that only the spectrum of an amorphous absorber is recorded with the Ge:^{73}As source indicates the proximity of the electronic structures of ^{73}Ge atoms in monocrystalline germanium (the atoms have a tetrahedral chemical bond system) and in the amorphous $Ge_2Sb_2Te_5$ alloy. This confirms the conclusion based on the MS data on ^{119}Sn impurity atoms about the stabilization of germanium atoms in the amorphous $Ge_2Sb_2Te_5$ alloy in tetrahedral coordination (Marchenko et al. 2023). It also indirectly confirms the conclusion (Marchenko et al. 2023) that there is a significant difference in the immediate environment and, consequently, the electronic structures of Ge atoms in crystalline and amorphous $Ge_2Sb_2Te_5$ films.

An attempt was made to establish correlations between the isomeric shifts of both Mössbauer isotopes to assess the possible position of the ^{73}Ge spectrum in the crystal film and to jointly interpret the MS results for the ^{73}Ge and ^{119}Sn isotopes. Calculations of the electron densities on the nuclei of Ge and Sn impurities in the same matrices, which show a linear correlation between these values, are a prerequisite for their search (Svane 1988).

In Fig. 2, these data are plotted on the axes isomeric shift ^{73}Ge (relative to crystalline Ge) IS_{Ge} — isomeric shift ^{119}Sn (relative to α-Sn) IS_{Sn} in silicon, germanium and copper matrices. Experimental data for ^{73}Ge are taken from (Pfeiffer, Kovacs 1981; Pfeiffer et al. 1983) and for ^{119}Sn from (Regel, Seregin 1984). In this case, the values of the ^{73}Ge isomeric shift in Si are plotted with both signs, as discussed above. They can be approximated by two linear functions:

$$IS_{Ge}\ (\mu m/s) = 2309 \times IS_{Sn}\ (mm/s) + 43.3 \quad (1)$$

$$IS_{Ge}\ (\mu m/s) = -2583 \times IS_{Sn}\ (mm/s) - 152.4 \quad (2)$$

The dotted line corresponds to the ratio (2) and the isomeric shift of ^{73}Ge in Si IS_{Ge} = –685 μm/s, while the solid line represents the ratio (1) and the isomeric shift of ^{73}Ge in Si IS_{Ge} = +685 μm/s.

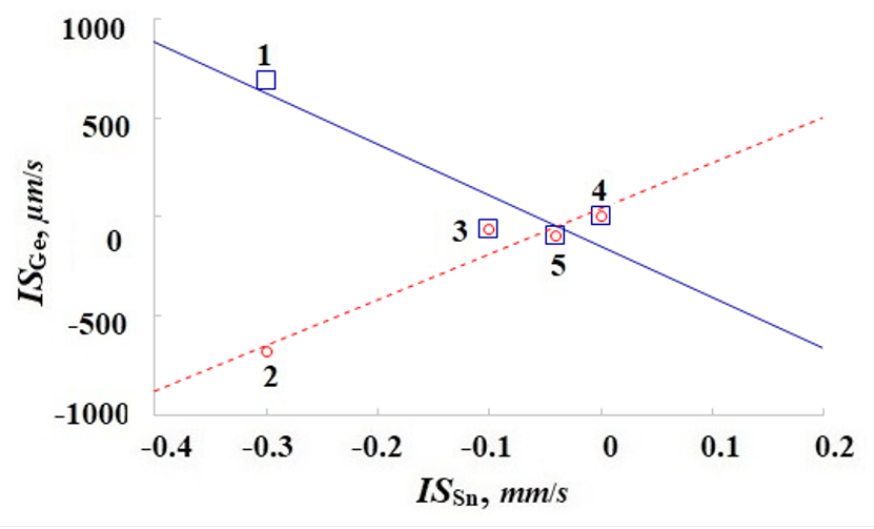

Fig. 2. Relations between isomeric shifts of the Mössbauer spectra of ^{119}Sn IS_{Sn} atoms (circles) and ^{73}Ge IS_{Ge} (squares) in monocrystalline silicon (1, 2), copper (3), germanium (5), and in an amorphous $Ge_2Sb_2Te_5$ film (4). Experimental data for ^{73}Ge are taken from (Pfeiffer, Kovacs 1981; Pfeiffer et al. 1983) and for ^{119}Sn from (Regel, Seregin 1984). The dotted line corresponds to the ratio (2) and the isomeric shift of ^{73}Ge in Si IS_{Ge} = −685 μm/s, while the solid line represents the ratio (1) and the isomeric shift of ^{73}Ge in Si IS_{Ge} = +685 μm/s

Thus, the choice of one of the ratios (1) or (2) is of no fundamental importance for estimating the range of assumed positions of the ^{73}Ge spectrum to the $Ge_2Sb_2Te_5$ crystal film. However, it may be important in determining the nuclear characteristics of ^{73}Ge. In particular, Svane assumed the ^{73}Ge isomeric shift in Si to be −685 μm/s, which corresponds to the ratio (2), and obtained a relative change in the charge radius upon transition to the level of 13.3 keV $\Delta R/R = 1.7 \times 10^{-3}$. If we use the value of the isomeric shift of ^{73}Ge in Si equal to +685 μm/s, then it leads to the ratio (1), which definitely indicates that the value of $\Delta R/R$ for ^{73}Ge should be considered equal to -1.9×10^{-3}.

Conclusions

Using Mössbauer spectroscopy on the ^{73}Ge isotope, we demonstrated the tetrahedral symmetry of the local environment of germanium atoms in amorphous $Ge_2Sb_2Te_5$ films, concluding that there is a significant difference both in the local symmetry of the nearest environment of germanium atoms and in their electronic structure in crystalline and amorphous $Ge_2Sb_2Te_5$ films.

The possibility of one of two relationships between the isomeric shifts of the Mössbauer spectra of ^{73}Ge and ^{119}Sn atoms in silicon, germanium, and copper has been established. Both ratios give the same absolute value of the isomeric shift of the Mössbauer ^{73}Ge spectrum in an IS_{Ge} polycrystalline film but at the same time lead to either its positive or negative sign. If we take IS_{Ge} to be negative, then the relative change in the ^{73}Ge charge radius upon transition to the 13.3 keV level turns out to be equal to $\Delta R/R = 1.7 \times 10^{-3}$. If we use a positive IS_{Ge} value, then the value of $\Delta R/R$ turns out to be equal to -1.9×10^{-3}.

Conflict of Interest

The authors declare that there is no conflict of interest, either existing or potential.

Author Contributions

A. V. Marchenko and P. P. Seregin formulated the research problem. V. A. Doronin synthesized the samples. Yu. A. Petrushin organized the measurement and processing of the experimental spectra. All authors contributed equally to the work by discussing the results and collaborating on writing the article.

 https://www.doi.org/10.33910/2687-153X-2025-6-3-139-143

References

Baker, D. A., Paesler, M. A., Lucovsky, G. et al. (2006) Application of bond constraint theory to the switchable optical memory material $Ge_2Sb_2Te_5$. *Physical Review Letters*, 96, article 255501. https://doi.org/10.1103/PhysRevLett.96.255501 (In English)

Bouzid, A., Ori, G., Boero, M. (2017) Atomic-scale structure of the glassy $Ge_2Sb_2Te_5$ phase change material: A quantitative assessment via first-principles molecular dynamics. *Physical Review B*, 96, article 224204. https://doi.org/10.1103/PhysRevB.96.224204 (In English)

Caravati, S., Bernasconi, M. (2007) Coexistence of tetrahedral- and octahedral-like sites in amorphous phase change materials. *Applied Physics Letters*, 91, article 171906. https://doi.org/10.1063/1.2801626 (In English)

Kolobov, A., Fons, P., Tominaga, J. et al. (2004) Understanding the phase-change mechanism of rewritable optical media. *Nature Materials*, 3 (10), 703–708. http://dx.doi.org/10.1038/nmat1215 (In English)

Liu, X. Q., Li, X. B., Zhang, L. et al. (2011) New structural picture of the $Ge2Sb_2Te_5$ phase-change alloy. *Physical Review Letters*, 106, article 025501. https://doi.org/10.1103/PhysRevLett.106.025501 (In English)

Marchenko, A. V., Terukov, E. I., Nasredinov, F. S. et al. (2023) Local structure of amorphous $(GeTe)x(Sb_2Te_3)$ films. *Technical Physics*, 68 (1), S88–S95. https://doi.org/10.1134/S1063784223090104 (In English)

Pfeiffer, L., Kovacs, T. (1981) Calibration of the isomer shift and measurement of $\Delta R/R$ for the 13-keV Mössbauer transition of ^{73}Ge. *Physical Review B*, 23, 5725–5728. https://doi.org/10.1103/PhysRevB.23.5725 (In English)

Pfeiffer, L., Kovacs, T., Celler, G. K. (1983) Mössbauer effect of ^{73}Ge in laser-processed Si and Ge crystals. *Physical Review B*, 27, 4018–4026. https://doi.org/10.1103/PhysRevB.27.4018 (In English)

Regel, A. R., Seregin, P. P. (1984) Mössbauer studies of impurity atoms in semiconductors. *Soviet Physics. Semiconductors*, 18, 723–740. (In English)

Stellhorn, J. R., Hosokawa, S., Kohara, S. (2020) Local- and intermediate-range structures on ordinary and exotic phase-change materials by anomalous X-ray scattering. *Analytical Sciences*, 36 (1), 5–9. http://dx.doi.org/10.2116/analsci.19SAR02 (In English)

Svane, A. (1988) Electronic structures and isomer shifts of Ge, Sn and Sb impurities in elemental semiconductors. *Journal of Physics C: Solid State Physics*, 21 (31), article 5369. https://doi.org/10.1088/0022-3719/21/31/008 (In English)